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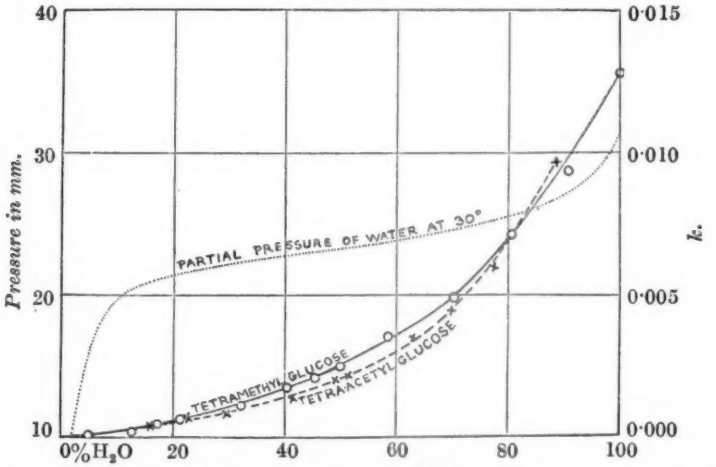
acetone upon the water or upon the other impurities which give rise to mutarotation in inert solvents. We therefore anticipated that, when mixed with water in various proportions, acetone would reduce the catalytic activity of the water more rapidly than its total concentration. The results recorded in Tables I and II show that this anticipation was amply fulfilled. Thus in a 50% mixture of acetone and water the velocity of mutarotation of tetramethylglucose is only about 20% of that in pure water. The water in this solution has therefore less than one-half of its normal activity in the free state.

We have also compared the velocity coefficients in Tables I and II with the partial vapour pressures of aqueous acetone at 30° as recorded by Makovetzki (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 226),

FIG. 1.



but can find no indication of any parallelism between them. In particular, the velocities shown in the figure appear to rise progressively from the origin at 0% H_2O, where the curves are perhaps tangential to the horizontal axis, whilst the dotted curve which shows the partial vapour pressure of water is inflected in the normal fashion for mixtures showing strong positive deviations from Raoult's law of lowering of vapour pressure. We therefore conclude that the catalytic activity of the water, which is obviously not proportional to its total concentration, is also not a simple linear function of its activity as measured by its partial vapour pressure above the solution.

EXPERIMENTAL.

The physical constants of the tetramethylglucose used in these experiments have already been given (J., 1925, **127**, 1387, footnote);

they are in close agreement with those recorded by Irvine. The purity of the sample is, however, guaranteed even more effectively by the arrest of mutarotation observed in several inert solvents; moreover, the mutarotation constants of the sugar were not altered appreciably by three further crystallisations from ether and from petrol:

	Specific rotation, $[\alpha]_{5461}$.			
	Initial.	Final.	Ratio.	Vel. coeff.
Before recrystallisation	117°	95°	1·23	0·0128
After „	115	94	1·23	0·0124

The tetra-acetylglucose was prepared for us by Messrs. Boots Pure Drug Co., Nottingham, to whom we wish to express our thanks for their generous gift. The substantial purity of the specimen was established by analysis, but we have not been able to find any trustworthy figures for the physical constants of the compound. The melting point, 118°, given by Fischer and Delbrück (*Ber.*, 1909, **42**, 2779) has no clear significance, since prototropic compounds have two different melting points, according as time is allowed for isomeric change to take place or not. In the case of tetra-acetylglucose we find that the true melting point, at which the compound melts in about 10 seconds when plunged into a bath heated to a known temperature, is 123°, as recorded by a standardised Anschütz thermometer graduated to 0·2°; and that the "equilibrium temperature" (Lowry, J., 1899, **75**, 233), at which the compound melts or re-melts when heated slowly, is 110°. Since a small specimen of tetra-acetylglucose given to us by Professor Haworth melted at the same temperatures, within less than a degree in each case, we feel justified in putting forward these temperatures as provisional standards, which can be verified by comparison with values recorded in the future for other specimens of the purified sugar. The rotatory powers given by Fischer and Delbrück, $[\alpha]_D^{22°} = +2{\cdot}19°$ to $+82{\cdot}7°$, were apparently determined at room temperature, with unpurified sodium light, and in alcohol of unspecified water content. We have not attempted to make any exact comparison with these uncertain data, but in our opinion the value $[\alpha]_{5461} = +6°$ for a 5% solution of tetra-acetylglucose in pure anhydrous acetone at 20° can be accepted provisionally as a characteristic constant of the unchanged sugar, since this value is permanent over a period of several hours. As in the case of tetramethylglucose, the purity of the sample used in our experiments was established most satisfactorily by the complete arrest of mutarotation which we have observed repeatedly in solutions of the sugar in an inert solvent. Since the suggestion has been made that the mutarotation of tetra-acetylglucose in aqueous acetone may be due in part to hydrolysis instead of to isomeric change, we have made direct experiments to test this point, but could

not detect any hydrolysis after a week at a temperature of about 18°; after 10 days, the proportion of sugar hydrolysed was only of the order of 0·5%. After 7 months, the residues from the original experiments were hydrolysed to the extent of only 5%. The hydrolysis of the sugar can therefore have had no perceptible influence on the velocity of mutarotation, a conclusion which we had already anticipated from the steadiness of the observed end-points, since it was incredible that hydrolysis (as well as isomeric change) could be complete in the course of a few hours or days.

The acetone had been purified through the compound with sodium iodide (J., 1913, **103**, 1255). The solutions were prepared by dissolving about 1 g. of tetramethylglucose, or 0·5 g. of tetra-acetylglucose, in 20 c.c. of an aqueous acetone made up by weighing. Tetramethylglucose was examined over the whole range of concentrations from 0 to 95% of acetone, but tetra-acetylglucose is almost insoluble in water and only slightly soluble in water containing 5% of acetone. A solution of the latter concentration was prepared by dissolving the sugar in acetone and adding the necessary quantity of water; but the constants of the mutarotation curve were unsatisfactory, and the values for this solution have not been included in the table. The very slow mutarotations in acetone containing only traces of water were not included in the present research. In order to economise space, all the individual readings have been omitted, but the unimolecular velocity coefficients for the various solutions are set out in Tables I and II, and are shown graphically in the figure.

TABLE I.

Mutarotation of Tetramethylglucose in Aqueous Acetone at 20°.

Acetone %.	Acetone, mols. %.	$k \times 10^5$.
0	0	1280
9·25	3·08	934
19·20	6·9	710
29·7	11·8	487
41·4	18·0	351
50·0	23·7	246
54·6	27·3	206
59·6	31·4	177
67·7	39·4	110
78·7	53·4	60
82·8	59·5	45
87·3	69·8	18·4
95·1	85·7	3·0

TABLE II.

Mutarotation of Tetra-acetylglucose in Aqueous Acetone at 20°.

Acetone %.	Acetone, mols. %.	$k \times 10^5$.
11·5	3·7	965
22·6	8·0	596
30·0	11·6	441
36·8	15·0	346
48·4	23·5	217
50·7	24·6	200
58·5	30·6	129
70·3	42·1	80
77·3	50·7	60
83·9	61·8	28

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[*Received, November 26th*, 1925.]

CI.—*Absorption Spectra of Condensed Nuclear Hydrocarbons.*

By Norman Stewart Capper and Joseph Kenneth Marsh.

It was shown recently that visible absorption bands attributed to anthracene were due to an impurity, chrysogen (*J. Amer. Chem. Soc.*, 1925, **47**, 2847). It has now been found that other coal-tar hydrocarbons have been insufficiently purified for spectroscopic examination. Thus the four chief hydrocarbons boiling between 275° and 360° cannot be separated by crystallisation, as they appear to form mixed crystals. In particular, fluorene and phenanthrene retain traces of anthracene, which can be detected by its intense ultra-violet absorption. The absorption bands of the purified substances exhibit constant frequency differences, which have been attributed to the double carbon bond in the aromatic series (Marsh, *Phil. Mag.*, 1925, **49**, 971, 1206). Other synthetic hydrocarbons also have been examined.

Purification of Phenanthrene and Fluorene from Anthracene.—A good commercial phenanthrene showed anthracene bands of an intensity corresponding with a content of about 16%, and this was not greatly reduced by fractional crystallisation. The melting point gives no trustworthy information as to the purity. In the fluorene used, the anthracene content was not more than 1 or 2%.

Purification of both substances was effected by refluxing a strong xylene solution by the heat from a silica mercury vapour lamp. The light caused the anthracene present to polymerise, even in glass vessels. Owing to its very slight solubility, the dianthracene produced was readily separated, but since anthracene and dianthracene attain to an equilibrium repeated light treatments and separations were necessary. About 1% of anthracene was thus eliminated from Kahlbaum's "purest reagent" phenanthrene. The spectra of the purified products examined in concentrated chloroform solutions indicated an anthracene content of about 0·01% in the phenanthrene and 0·001% in the fluorene. The melting point of the fluorene was 114—114·5°, a value higher than that commonly accepted. The phenanthrene melted at 98°. The higher values usually quoted probably result from the eutectic mixture with anthracene containing very nearly 100% of phenanthrene. The purified material in both cases lost its visible fluorescence, even in strong actinic light, or in the case of phenanthrene at most only a slight trace remained.

The absorption spectra were studied with a Hilger spectrophotometer and condensed copper spark. Little description will be

necessary if the absorption curves, the photographic reproductions, and the table of band positions are examined.

Phenanthrene.—Previous spectroscopists have used specimens containing from 0·3% (Baly and Tuck, J., 1908, **93**, 1902) to upwards of 10% of anthracene, masking completely the true spectrum, which in the region above 3000 Å. is some 25 times weaker than that of anthracene. Probably the small narrow band recorded at about 1/λ4000 is due to the remaining trace of anthracene, and a very faint band at 1/λ3120 to acenaphthene.

Fluorene.—A band found at 1/λ3117 may be ascribable to the presence of 1% of acenaphthene.

Anthracene, 9-phenylanthracene, and 1 : 2-benzanthracene have very similar spectra. Relatively to those of anthracene, 9-phenylanthracene has its bands shifted about 60 units towards the visible spectrum, and they are not so distinct. In 1 : 2-benzanthracene, the weaker member of each pair appears on the red side of the strong band, but the first pair is very weak. In the middle ultraviolet, bands corresponding to those found in phenanthrene are seen. The structure may be regarded as 2 : 3-benzphenanthrene.

On examining anthracene vapour (20 cm.) at 50° to 120°, both of the strongest bands were seen to have a weak neighbour on each side, and there was also a faint band midway between the two strong ones. The bands were shifted almost 100 units with respect to their solution positions.

Octahydroanthracene lacks entirely the set of bands above λ3000 found in anthracene, but has several at about 1/λ3500 to 3700, *i.e.*, in the same region as those in other alkyl derivatives of benzene.

Bisdiphenylene-ethylene, $(C_6H_4)_2C{:}C(C_6H_4)_2$, showed only a broad band in the blue region, an undeveloped one at about 1/λ3600, and another at about 4100.

Chrysogen.—This substance of unknown structure occurring in small quantities—probably less than 0·1%—in most samples of anthracene has an anthracene nucleus, since it is capable of polymerising similarly to anthracene itself. Its spectrum is distinctly of the polynuclear hydrocarbon type. In fused anthracene the band positions are 60—80 Å. nearer the red end of the spectrum.

Other Polynuclear Hydrocarbons.—In the substances examined, except fluorene and octahydroanthracene, every carbon atom has an unsatisfied valency, and except for bisdiphenylene-ethylene the unsaturation is entirely aromatic in character. Leaving aside these three, the chief feature of the spectra is a series of rather narrow bands between λλ3000 and 4000, which show a constant frequency difference of about 142 waves/mm. Previous workers have examined other hydrocarbons which come into the same

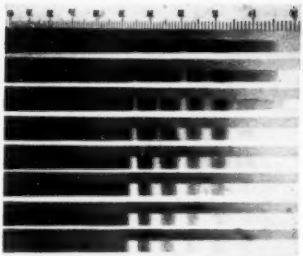
category. These substances also exhibit narrow bands, although the interval may vary. The absorption bands of benzene vapour are spaced 92·4 units apart (Henri, *J. Phys. Radium*, 1922, **3**, 181) and the emission bands at 98·7 unit intervals (J., 1923, **123**, 642). Naphthalene vapour shows a long series of bands, both absorption (Henri and László, *Proc. Roy. Soc.*, 1924, *A*, **105**, 662) and emission (Dickson, *Z. wiss. Photochem.*, 1912, **10**, 166), at 47·4 unit intervals. The emission spectrum shows every third band stronger than its neighbours, making an interval of 142 as in anthracene, etc. Baly and Tuck found in chrysene (J., 1908, **93**, 1902) four bands as nearly as can be determined at 140 unit intervals. A partial examination of picene, 2 : 3 : 6 : 7-dibenzanthracene, and ββ-dinaphthyl was made by Homer and Purvis (J., 1908, **93**, 1319).

Table of Bands.

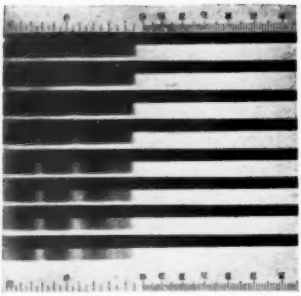
The figures are oscillation frequencies, and in italics are the frequency intervals. Small bands detected but difficult to locate accurately have been omitted.

Anthracene.	2661	2701	2804	2844	2947	2994	3090
		143		*143*		*143*	
			103		*103*		*96*
	3133	3231	3231	3373	3960	4058	
	141			*142*	*6×98*	*98*	
		98					
Vapour.	2725	2759	2797	2830	2864	2899	2934
(2759 and 2899 correspond to solution bands 2666 and 2804.)							
Phenanthrene.		2895	2958	3033	3100	3171	3243
			138		*138*		*140*
				142		*142*	
		3415	3555	3654	3787	3990	4132
		140	*99*		*2×101*	*142*	
9-Phenylanthracene.		2603	2743	2883	3024	3917	
		140	*140*	*141*			
1 : 2-Benzanthracene.		2599	2670	2740	2787	2826	
			140			*143*	
		2930	3070	3339	3479		
		140		*140*			
Chrysogen.		2105	2247	2389			
		142	*142*				
Fluorene.		3117 ?	3333	3426	3820		
Octahydroanthracene.		3268	3333	3506	3580	3629	3686
Bisdiphenylene-ethylene.		2190	3610	4130	(All broad and indefinite)		

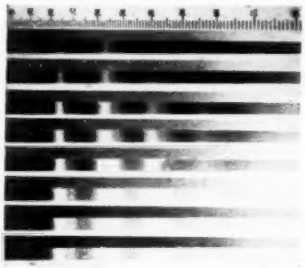
Benzene and the other eight condensed nuclear hydrocarbons all have the same type of multiple narrow-banded spectra, the main intervals being generally 142 units in the heavier molecules, 142 or 142/3 in naphthalene, and $142 \times \frac{2}{3}$ in benzene. The simple methyl and other derivatives may also give spectra consisting of



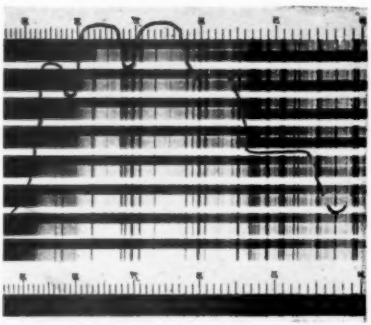
Phenanthrene. 1 cm. $M/200$.



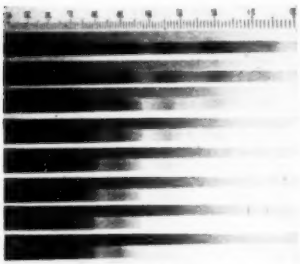
Chrysogen in 4 cm. of $M/10$-anthracene.



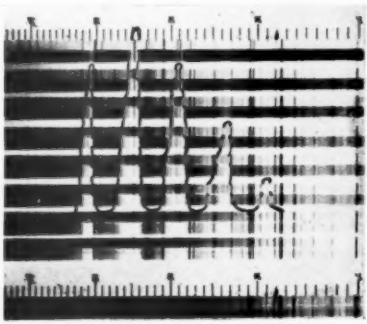
Anthracene. 1 cm. $M/5000$.



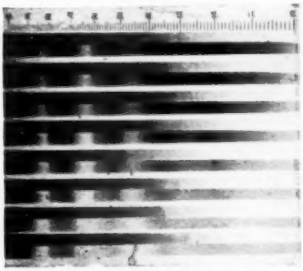
Naphthalene. 1 cm. $M/5000$.



1 : 2-Benzanthracene.
1 cm. $M/5000$.



Benzene. 1 cm. $M/200$.

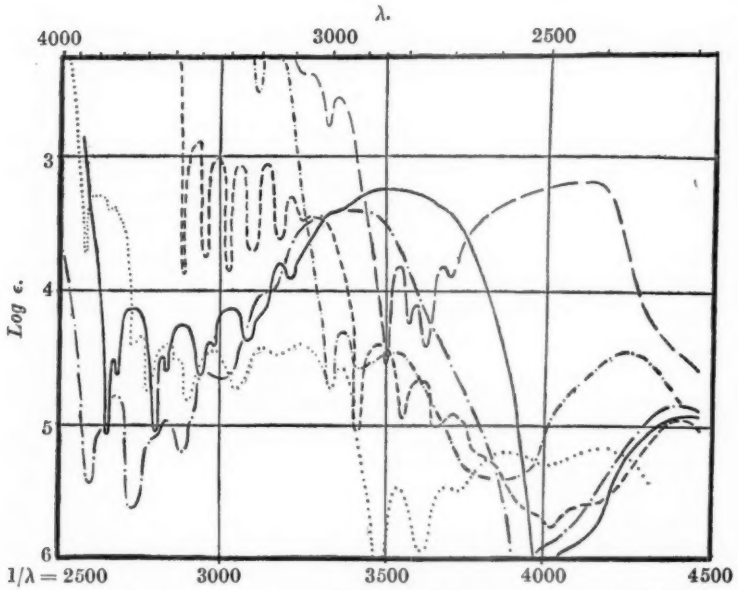


9-Phenylanthracene.
1 cm. $M/5000$.

[*To face p.* 726]

a number of narrow bands, but the regularity and sharpness are usually less marked, *e.g.*, László (*Z. physikal. Chem.*, 1925, **118**, 369) finds band series at the intervals 154, 142·5, 147, and 138, for 1-methyl-, 2-methyl-, 2 : 7-dimethyl-, and 2 : 6-dimethylnaphthalene, respectively. In phenanthrene alternate bands are similar and show the interval 142, the intermediate ones being not quite centrally situated.

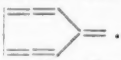
FIG. 1.



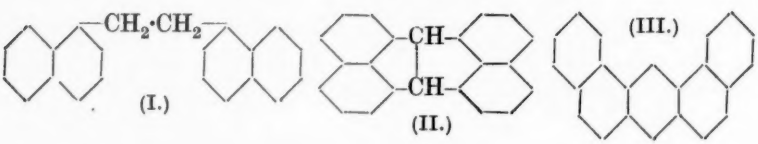
Besides the series of five or six bands already mentioned, most of the substances give other bands farther in the ultra-violet and of greater intensity. There is usually one well marked, with, on the more refrangible side, other less distinct bands, again at intervals of 142 units. Phenanthrene and 2 : 3-benzphenanthrene (1 : 2-benzanthracene) have also a third intermediate region.

Discussion of Results.

By removing all anthracene from phenanthrene and fluorene, entirely new absorption curves for these two substances have been found. Fluorene now gives a spectrum similar to that of *o*-xylene or other simple substituted benzene derivative. Phen-

anthrene presents a spectrum differing from that of anthracene in strength, band position, and arrangement. Hyatt (*Physical Rev.*, 1922, **19**, 391), employing the same methods as ours, measured 16 bands for anthracene. Three of these not now observed were possibly due to phenanthrene. We do not find that the remainder can be divided into a series at intervals of 147 and another at 142. *Both* our series run at intervals of 142. The spectral type of bis-diphenylene-ethylene differs completely from that of the other polynuclear hydrocarbons. The strong red colour is associated with the ethylenic bond, disappearing on its reduction, and it constitutes with its neighbours the characteristic system of the visibly coloured fulvenes,  .

The spectrum of stilbene, the simplest example of a substance containing an ethylenic bond between benzene nuclei, consists of a single broad band at about λ3300 : in phenanthrene this double bond becomes aromatic, and half-a-dozen narrow bands occupy the same region. Thus the effect of an ethylenic bond is to cause the fusion of the aromatic bands. Another substance having an absorption curve very similar to those of bisdiphenylene-ethylene and stilbene and in a position intermediate between them was examined by Purvis and Homer (J., 1909, **97**, 1155). It was a product of the reaction between tetrabromoethane and naphthalene. They concluded, largely on spectroscopic evidence, that it was 1 : 2 : 7 : 8-dibenzanthracene. Its spectrum, however, is entirely different from what we have found for 1 : 2-benzanthracene and would be the only deviation from the type characteristic of the class of substances to which their formula would relegate it. Ethylene dibromide and naphthalene were considered to give rise to *s*-di-α-naphthylethane (I), which then broke down to picene. Tetrabromoethane and naphthalene might therefore give rise to the substance (II), and this would be much more likely to give a spectrum with broad bands than would a substance having the suggested formula (III).



Relationship to Infra-red Spectra.—It does not seem possible to offer any detailed explanation of the differences which make all these closely related spectra individually characteristic, but the cause of the similarity constituting the spectral type found in this

group of hydrocarbons must be some common factor, and therefore one or more of the following: (*a*) a benzene ring, (*b*) a C=C linking, (*c*) a CH: group. These possibilities will be considered with reference to the known features of the infra-red spectra of these or similar substances. Coblentz (*Carnegie Inst. Publication*, No. 35, 1905), from a study of some thirty hydrocarbons, concluded that characteristic absorption maxima due to methyl and methylene groups are found at 3·43, 6·86, 13·6—13·8, and 14 μ. Weniger (*Physical Rev.*, 1910, **31**, 388) gives also a band at 7·3 μ. In the aromatic series, Coblentz gives the following bands as characteristic of benzene: 3·25, 6·75, 8·68, 9·8, 11·8, and 12·95 μ. The first two and the last are identifiable with bands in hydrocarbons of the aliphatic series, but, owing to the unsaturation of the carbon atom of the CH: group, their frequency is increased somewhat. Thus the 3 μ band has the value 3·08 for acetylene, 3·25 for benzene, 3·28 for ethylene, and 3·39 for ethane.

The strongest bands of ethylene are:

λ	$\binom{21}{47\cdot6}$	10·5	6·98	5·3	3·28
1/λ		95·24	143·3	188·9	304·9
Diff.	47·6	48·1	45·6	—	

Except the last, these are evidently multiples of a band which should occur at 1/λ47·6, and may be considered as due to C:C. In benzene vapour, is a series of bands at intervals of 15·9, *i.e.*, 47·6/3; in naphthalene, the series interval is 47·4 and in the heavier hydrocarbons 142, *i.e.*, 47·4 × 3. The ethylene band 6·98 μ occupies also the position of a CH-band. The fifteen aliphatic hydrocarbons examined by Coblentz show, as consistently the most prominent in their spectrum, two bands at about 6·86 and 7·33 μ. The frequencies (145·8—136·4 waves/mm.) are just what are found to be the intervals between the ultra-violet bands of the polynuclear hydrocarbons. Experimental difficulties have prevented thorough investigation of the infra-red spectra of the solid aromatic hydrocarbons. Stang (*Physical Rev.*, 1917, **9**, 342), however, has examined naphthalene and several of its derivatives and finds a band at 7·19 μ (1/λ139·1) to be among the strongest in the spectrum. It remains therefore an open question as to whether this common frequency difference is due to CH: or C:C, but probably it is a frequency to which both can resonate and for this cause it dominates the infra-red and ultra-violet spectra. Indeed, if any sort of harmonic motion is to be preserved in the molecule, it is necessary that different oscillations should be in tune with one another, and that the relative frequencies must be expressible as whole numbers.

We are much indebted to Mr. E. de B. Barnett for supplying very pure samples of the three anthracene derivatives examined.

THE SIR DONALD CURRIE LABORATORIES, QUEEN'S UNIVERSITY, BELFAST, NORTHERN IRELAND. [*Received, December 5th*, 1925.]

CII.—*The Interaction of Nitric Oxide and Hydrogen and the Molecular Statistics of Termolecular Gaseous Reactions.*

By CYRIL NORMAN HINSHELWOOD and THOMAS EDWARD GREEN.

THE only known termolecular gaseous reactions are :

$2NO+Cl_2 = 2NOCl$ (Trautz, *Z. anorg. Chem.*, 1914, **88**, 285).

$2NO+Br_2 = 2NOBr$ (Trautz and Dalal, *ibid.*, 1918, **102**, 149).

$2NO + O_2 = 2NO_2$ (Bodenstein, *Z. physikal. Chem.*, 1922, **100**, 68).

We have succeeded in measuring a homogeneous change between nitric oxide and hydrogen in the region of 1100° Abs., which proceeds in accordance with the equation

$$-d[NO]/dt = k[NO]^2[H_2] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and is thus termolecular.

The ultimate result of the interaction being expressed by the equation

$$2NO + 2H_2 = N_2 + 2H_2O,$$

it must be supposed that the action takes place in stages thus,

$$2NO + H_2 = N_2 + H_2O_2$$
$$H_2O_2 + H_2 = 2H_2O$$

or

$$2NO + H_2 = N_2O + H_2O$$
$$N_2O + H_2 = N_2 + H_2O,$$

the second stage in either of the alternatives being a rapid reaction subsequent to the main change of which the speed is measured.

There are reasons why this new reaction possesses considerable interest. These may be briefly outlined as follows.

The majority of known gaseous reactions are bimolecular. The application of the kinetic theory of gases leads to a simple explanation of these. The molecules which react are those which collide while they possess the " energy of activation," which can be found from the temperature coefficient of the reaction velocity. When the total number of collisions taking place in unit time is multiplied by $e^{-E/RT}$, a fraction representing the chance that the energy of the colliding molecules shall exceed the energy of activation, E, a number is obtained which is very nearly equal to the number of

molecules which actually undergo chemical transformation. Thus the possession of the energy of activation seems to be the only important factor in bimolecular reactions. Since the number of collisions depends on the molecular diameter, and since all molecular diameters are of the same order, 10^{-8} cm., the rate of a bimolecular change is chiefly determined by the value of $e^{-E/RT}$. We find, therefore, that different bimolecular reactions attain approximately equal rates at temperatures which make E/RT respectively the same for each (Hinshelwood and Hughes, J., 1924, **125**, 1841; Hinshelwood and Thornton, *Phil. Mag.*, 1925, **50**, 1135).

A bimolecular gaseous reaction which takes place with conveniently measurable velocity in the neighbourhood of 350° Abs. will have a heat of activation of about 20,000 calories, at 700° Abs. about 40,000 calories, and one which attains an equal speed at 1000° Abs. will have a value of about 60,000 calories. No exception is known to this rule, so that if we know the rate of a bimolecular reaction at a given temperature we can form a fairly accurate estimate of the heat of activation.

From the point of view of the molecular statistics of chemical change termolecular reactions are of special interest, since they depend on the rather rare event of a collision between three molecules. Bodenstein estimates the frequency of termolecular collisions to bear about the same proportion to the frequency of bimolecular collisions as the molecular diameter bears to the mean free path. At atmospheric pressure, the mean free path is of the order 10^{-5} cm., and since the molecular diameter is of the order 10^{-8}, ternary collisions should be about 1000 times less frequent than binary collisions. Thus if we have a bimolecular reaction and a termolecular reaction with equal heats of activation, the rate of the termolecular reaction should be at least 1000 times smaller than that of the bimolecular reaction at the same temperature. It will probably be more than 1000 times slower, since a considerable number of the ternary collisions are likely to be ineffective simply on account of unfavourable orientation of the molecules during impact. Taking this into consideration, it appears that the factor may be nearer 10,000.

Conversely, if a termolecular reaction and a bimolecular reaction were to take place at equal rates at the same temperature, then the heat of activation of the termolecular reaction would need to be the smaller by an amount ΔE, such that $e^{\Delta E/RT} = 1000$ to 10,000. Thus, other things being equal, the heats of activation of termolecular reactions ought to be about 5000 calories less at the ordinary temperature and about 15,000 calories less at 1000° Abs. than those of bimolecular reactions.

A bimolecular reaction which would take place at a rapid but measurable rate at the ordinary temperature would have a heat of activation of 12,000 to 15,000 calories, a termolecular reaction might therefore be expected to have one of 5000 to 10,000 calories. This would mean a very small temperature coefficient. Another factor enters, however, in this case, for Bodenstein found that the reaction $2NO + O_2 = 2NO_2$, instead of having a small positive temperature coefficient, had actually a very small negative temperature coefficient. This he attributed to the diminished " duration of collisions " at higher temperatures, which decreases the chance that two molecules shall still be within molecular distance of each other when a third approaches to complete a ternary collision. This factor is enough just to invert the small positive temperature coefficient which would otherwise be found. The other two termolecular reactions have in fact very small positive temperature coefficients. This new factor, therefore, is equivalent to the reduction of the apparent heat of activation by 5000 calories or so.

Trautz has an alternative explanation of Bodenstein's result. The reaction is supposed to be a bimolecular one between N_2O_2 and O_2. But since $[N_2O_2]$ is proportional to $[NO]^2$, the reaction is kinetically termolecular. The negative temperature coefficient is due to the increasing dissociation of N_2O_2 at higher temperatures. The apparent heat of activation would thus be equal to the difference between that of the bimolecular reaction between N_2O_2 and O_2 and the heat of dissociation of N_2O_2; and actually this difference comes out to be a small negative quantity.

Whichever way of regarding the matter is preferred—and there is not really much difference between the transitory existence of N_2O_2 and a collision of finite duration between two molecules of NO —it is clearly of interest to examine the behaviour of a termolecular reaction which takes place at a much higher temperature, say in the neighbourhood of 1000° Abs. A bimolecular reaction which proceeded at a conveniently measurable speed at this temperature would have a heat of activation of approximately 60,000 calories. A termolecular reaction should therefore have one about 20,000 calories less.

The predicted heat of activation is thus about 40,000 calories. We find actually the heat of activation of the termolecular reaction between nitric oxide and hydrogen to be 44,000 calories. This result seems to show that termolecular reactions can be interpreted satisfactorily in terms of the simple kinetic theory, and to provide further evidence that the energy of activation is a quantity with a real physical meaning.

It is perhaps significant that the four termolecular reactions now

known all involve the participation of two molecules of nitric oxide. It may be simply coincidence, or it may be that the "duration of collision" is greater in encounters between molecules of nitric oxide than in encounters between other molecules, so that there is more chance of the third molecule arriving in time. Some may prefer to call this phenomenon, assuming it to be a real one, formation of N_2O_2.

Preparation of the Gases.—The hydrogen used was electrolytic and was purified from oxygen by passage over a hot platinum wire; it was then dried with phosphoric oxide. The nitric oxide was prepared in a state of purity by the "nitrometer" reaction and stored in contact with concentrated sulphuric acid in the vessel in which it was made.

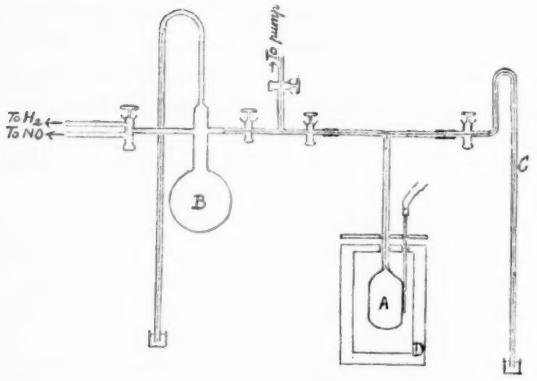
Apparatus and Method of Measurement.—Since the reaction is attended by a decrease in pressure, a simple manometric method can be employed. It is necessary, however, to prevent the condensation of the steam which is produced. This was done in the following way. The reaction vessels were of clear fused silica, 260 c.c. and 155 c.c. in capacity, respectively. The bulb was sealed to a long T-piece of fine silica capillary tube, which communicated with the manometer. The whole of this T-piece was heated to about 140°. Under these conditions, when the reaction took place in the heated bulb, no water vapour diffused through the length of capillary tube and condensed in the cooler part of the apparatus such as the capillary of the manometer itself. The silica capillary tube was joined to the glass parts of the apparatus by means of stout rubber joints. It was arranged that the silica and the glass made good contact beneath the joints, and careful observation showed that no disturbance of any kind arose from the presence of these. They were quite cold. The escape of hydrogen through the walls of the silica bulb at the temperature of the experiments was known from independent experiments to be negligible.

The arrangement of the apparatus is obvious from Fig. 1. *A* is the reaction bulb, heated in an electric furnace, the temperature of which was controlled by a thermo-couple and kept constant to about a degree by hand regulation of the heating current. The thermo-couple was standardised as described in previous papers (J., 1924, **125**, 393). *B* is a reservoir in which the gases could be mixed before being allowed to stream into the reaction vessel. In some of the experiments it was omitted.

It was ascertained by direct experiment that the reaction tended asymptotically to the theoretical "end-point" and that diffusion of water vapour from the heated region did not occur during the time of an ordinary experiment.

Kinetics of the Reaction.—The main series of experiments were made at 826° C. This approaches the highest temperature at which experiments can be made accurately. The conclusions drawn about the nature of the reaction are as follows. It is almost entirely homogeneous at higher pressures, and is of the third order, its rate being proportional to the square of the pressure of the nitric oxide and to the first power of that of the hydrogen. At lower pressures, where the reaction is slower, it is less exactly of the third order, and, moreover, the straight line obtained by plotting the initial rate of reaction against the pressure of hydrogen does not pass exactly through the origin. These facts indicate that a certain amount of heterogeneous reaction takes place concurrently with

FIG. 1.



the homogeneous reaction. The heterogeneous change, as would be expected from the strong adsorption of hydrogen by silica, is probably almost independent of the hydrogen pressure. This assumption would explain also the failure of the reaction to follow the equation of a third-order reaction exactly at the lower pressures. These conclusions are confirmed by the addition of powdered silica to the reaction vessel to test for the existence of a surface reaction. There was found to be some, but it accounted for a small fraction only of the total change.

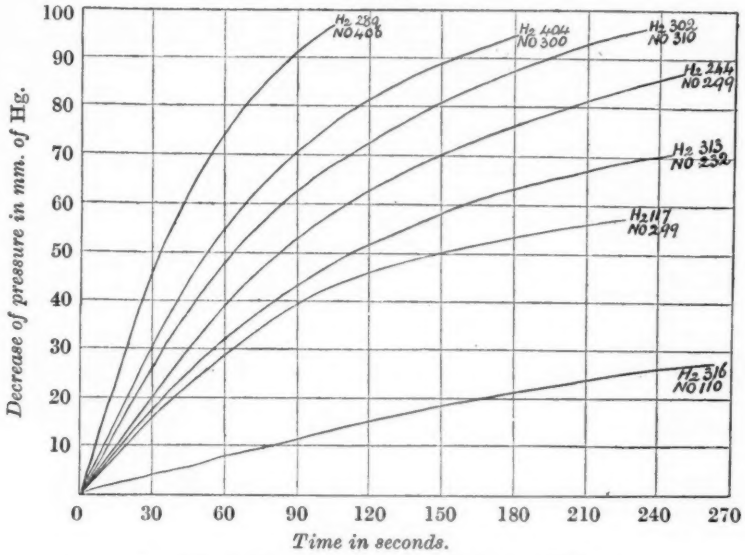
The results were very satisfactorily reproducible. For example, experiments 4, 5, and 31 of the whole series, which were made with the same pressures of nitric oxide and hydrogen, respectively, gave almost exactly superposable curves. This is in pleasing contrast with what is found when the reaction is one which takes place on the surface of the silica. A typical experiment is recorded below and others are shown in the curves of Fig. 2.

Temp. 826°. Initial pressure of NO = 406 mm. Initial pressure of H_2 = 289 mm., t is the time in seconds, and x the change of pressure in mm.

t	.....	8	13	19	26	33	43	54	69	87	110	140	204	310	∞
x	.....	10	20	30	40	50	60	70	80	90	100	110	120	127	144·5

The Order of the Reaction.—The following experiments were made with equimolecular amounts of nitric oxide and hydrogen. τ is the time in seconds required for half the reaction to complete itself,

FIG. 2.



Interaction of nitric oxide and hydrogen at 826° C.

Since the rate of reaction depends upon the square of the NO *concentration but the first power only of the* H_2 *concentration, a high pressure of nitric oxide has much more effect than a high pressure of hydrogen.*

a is the initial pressure in mm. of each gas, and n is the reaction order calculated from the equation $(a_1/a_2)^{n-1} = \tau_2/\tau_1$.

a_1.	τ_1.	a_2.	τ_2.	n.
354	81	202	224	2·81
340·5	102	288	140	2·89
340·5	102	243	176	2·62
375	95	251	180	2·60

The reason why n falls a little under 3·0 will be discussed below.

Influence of the Pressure of the Separate Gases.—(a) *Nitric oxide.* Experiments were made in which a fixed initial pressure of hydrogen was used and various initial pressures of nitric oxide. Curves were plotted on a large scale and the initial rate of reaction was found by drawing tangents. The following figures show that the rate is

proportional to the square of the nitric oxide concentration. The initial pressure of hydrogen was 400 mm. in each instance.

[NO]. (mm.).	[NO]. Relative.	$[NO]^2$. Relative.	Rate of reaction. (mm./100 sec.).	Rate of reaction. Relative.
359	2·38	*5·57*	150	*6·00*
300	1·98	*4·12*	103	*3·92*
152	1·00	*1·00*	25	*1·00*

A corresponding series of experiments made with a fixed initial pressure of hydrogen equal to 300 mm. gave the results

[NO]. (mm.).	[NO]. Relative.	$[NO]^2$. Relative.	Rate of reaction.	Rate of reaction. Relative.
400	1·73	*3·00*	174	*3·86*
310	1·34	*1·80*	92	*2·05*
232	1·00	*1·00*	45	*1·00*

(b) *Hydrogen.* In one series of experiments the initial pressure of nitric oxide was 400 mm.

$[H_2]$ (mm.).	$[H_2]$. Relative.	Rate of reaction (mm./100 sec.).	Rate of reaction. Relative.
289	*1·97*	160	*2·02*
205	*1·39*	110	*1·39*
147	*1·00*	79	*1·00*

In the second series, the pressure of nitric oxide was 300 mm. [The reaction is slower in the ratio $(300/400)^2$ for equal hydrogen pressures.]

$[H_2]$	404	302	244	147	117	104
Rate of reaction	103	85	72	59	52	45

These figures give a straight line when plotted, but the line does not pass exactly through the origin. The explanation of this lies in the fact that there is a small amount of surface reaction nearly independent of the pressure of hydrogen. This is what makes the experimentally determined order of reaction slightly less than 3·0. The effect is scarcely noticeable when there is a high pressure of nitric oxide, so that the speed of the gas reaction is great.

Influence of the Reaction Products.—We propose to investigate further the influence of inert gases on the rate of reaction. A preliminary investigation of the effect of the reaction products, steam and nitrogen, was made in the following way. Pairs of experiments were selected in which the nitric oxide and hydrogen were present in equimolecular proportions. A curve showing the amount of change at different times was first plotted from the results of the experiment in which the initial pressure was the greater. A point on this curve could be found at which the pressures of unchanged nitric oxide and hydrogen were the same as the initial pressures in the experiment with smaller initial pressures. This point was

used as the origin in plotting the results of the second experiment. The two curves proceeding from the new origin corresponded to reactions taking place under exactly the same conditions except that in one known amounts of the reaction products were present initially. In general, the curves nearly coincided; if anything, the products had a very slight accelerating influence, but it cannot be described as a first-order effect.

The Termolecular Velocity Coefficients.—The reaction follows the equation (1). If a is the initial pressure of nitric oxide and b that of hydrogen, this becomes

$$dx/dt = k(a - x)^2(b - x),$$

whence

$$kt = \frac{1}{(a-b)^2} \log \frac{b(a-x)}{a(b-x)} + \frac{1}{(a-b)}\left\{\frac{1}{a} - \frac{1}{a-x}\right\}$$

It is convenient to record results in terms of the period of half-change, τ. If hydrogen is in excess, half-change corresponds to $x = a/2$. Thus

$$k = \frac{1}{\tau}\left\{\frac{1}{(b-a)^2} \log\left(\frac{b}{2b-a}\right) + \frac{1}{a(b-a)}\right\}$$

When nitric oxide is in excess, half-change corresponds to $x = b/2$. Then

$$k = \frac{1}{\tau}\left\{\frac{1}{(a-b)^2} \log\left(\frac{2a-b}{a}\right) + \frac{1}{(b-a)}\left(\frac{b}{a(2a-b)}\right)\right\}.$$

Finally, when the two gases are in equimolecular proportions, $k = 3/(2\tau a^2)$.

The following table shows the constancy of k when [NO] and [H_2] are varied considerably. The temperature was 826° C.

[NO].	[H_2].	τ (secs.).	$k \times 10^7$.	[NO].	[H_2].	τ (secs.).	$k \times 10^7$.
299	244	112	1·24	110	316	270	1·19
310	302	129	1·19	152	404	204	0·91
300	404	100	1·09	359	400	89	1·12
293	402	100	1·11	144	323·5	227	1·10
406	289	57	1·21	298	280	125	1·35
402	201	46	1·23	181	209·5	264	1·39
405	147	50	1·06	378	376	98	1·08
404	209	49	1·21	370	376	92	1·17
299	147	66	1·60	253	250	180	1·31
175·5	208·5	254	1·50	340·5	340·5	102	1·27
178	220	238	1·45	243	243	176	1·44
232	313	152	1·19	288	288	140	1·29

The increase in k at lower pressures is due to the existence of the small amount of heterogeneous reaction.

Influence of Surface.—The results already described lead us to suspect that a certain amount of surface reaction goes on concurrently with the gaseous change. A series of experiments was

made in a smaller silica bulb containing some powdered silica. A summary of these is given below. The temperature was 826° as before.

Av. value of k for expts. in which [NO] and [H_2] were both greater than 300 mm.	$1{\cdot}18 \times 10^{-7}$
Compare av. value for larger, empty bulb	$1{\cdot}17 \times 10^{-7}$
Av. value of k for expts. in which [NO] and [H_2] were both greater than 200 mm. but not greater than 300 mm.	$1{\cdot}66 \times 10^{-7}$
Compare av. value for corresponding expts. with the empty bulb	$1{\cdot}30 \times 10^{-7}$

This confirms our conclusions, and indicates that at pressures above 300 mm. of each gas the reaction is almost entirely homogeneous.

The smaller bulb was now packed nearly half full with powdered silica. Its catalytic activity towards the decomposition of ammonia —a typical heterogeneous reaction—was about twenty to thirty times greater than that of the larger, empty bulb used in the main series of experiments. At a pressure of 270 mm. of nitric oxide and of hydrogen, the value of k was now found to be $2{\cdot}5 \times 10^{-7}$, or about doubled, as compared with the twenty- to thirty-fold increase produced in the rate of decomposition of ammonia. The heterogeneous reaction must therefore be a small part of the whole change. These results can only be regarded as qualitative, since the catalysis of the ammonia decomposition is very erratic and cannot be taken as a strictly quantitative measure of the surface area. At temperatures about 100° lower, the surface reaction was relatively slightly more in evidence, but not very markedly so.

Influence of Temperature.—Three series of experiments were made, two series with the empty bulb, of which the second is the better, since the pressures were higher in all the experiments (greater than 300 mm.), and a third series in the smaller bulb packed with powdered silica. The object of the last series was to find how the proportion of surface reaction varied with temperature, and thus discover what error, if any, would be introduced into the value for the heat of activation determined from the experiments made in the empty bulb.

The first series extended over a range of seven temperatures from 652° to 834° C. The value of E was found to be 42,000 calories. The Arrhenius equation was used in the usual manner.

The results of the second series are given below.

t° C.	826°	788°	751°	711°	683°	631°
k' (av.)	476	275	130	59	25·3	5·3

k' is the velocity coefficient expressed, not as before with the concentrations in mm., but with these converted into gram-molecules per litre. The time is in seconds. By plotting log k against the reciprocal of $(t + 273)$ a value of E is found equal to 44,000

calories. This second value is the better. We adopt it rather than the average value 43,000.

The third series gave the results

t	827°	785°	745°	718°	684°
k'	1446	692	415	280	90

From these the value found for E is 39,000 calories. In these last experiments rather more than half the reaction was probably heterogeneous, yet the value of E was only changed from 44,000 to 39,000 calories. Hence we may conclude that the correction to be applied to the value 44,000 for the small fraction of surface reaction is negligible.

Conclusion.—We may therefore conclude that the reaction which takes place at 826° C. between nitric oxide and hydrogen is almost entirely in the gaseous phase, and that the velocity coefficient of the homogeneous reaction is within 10% of $1{\cdot}0 \times 10^{-7}$ when the concentrations are expressed in millimetres of mercury and the time in seconds. The heat of activation of the gaseous reaction is 44,000 calories. We consider that it is justifiable to use these values in considerations of the molecular statistics of the reaction. From this point of view the reaction possesses much interest. But the presence of some surface reaction makes it rather unsuitable for studies much more detailed than the general one we have described. We are now investigating the catalytic reaction at the surface of platinum.

Summary.

The interaction of nitric oxide and hydrogen in the region 1000° to 1100° Abs. is a termolecular reaction proceeding in accordance with the equation $-d[NO]/dt = k[NO]^2[H_2]$. At pressures above 300 mm. of each of the gases, it is almost entirely homogeneous, but there is a small amount of surface reaction which becomes relatively more important at lower pressures. The heat of activation of the gaseous reaction is 44,000 calories. The molecular statistics of termolecular gaseous reactions are discussed from the point of view of the theory of activation.

It is pointed out that all the termolecular gaseous reactions now known involve the participation of two molecules of nitric oxide.

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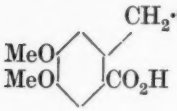
[*Received, December 22nd,* 1925.]

CIII.—*Synthetical Work on the* iso*Quinoline Alkaloids. Part I. Substituted* o*-Carboxyphenylethylamines.*

By GEORGE ALFRED EDWARDS.

THIS communication is concerned with the preparation and properties of substances obtained in a preliminary investigation of possible methods of preparing β-(4 : 5-dimethoxy-2-carboxyphenyl)ethylmethylamine (I), and of similar substances required in connexion with proposed syntheses of alkaloids of the cryptopine type.

Laudanosine appeared to be a possible source of this amino-acid, since Pyman (J., 1909, **95**, 1272) had shown that the lactam, 6 : 7-dimethoxy-2-methyldihydro*iso*quinolone (II), was obtained by its oxidation. He further showed that on more gentle oxidation



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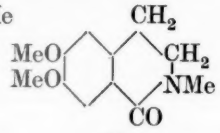

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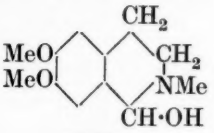
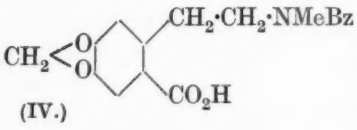


(III.)

1-hydroxy-6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline (III) was produced, and that it reacted in many respects like hydrastinine, which differs from it structurally only in containing the methylenedioxy-group in place of the two methoxy-groups. Freund (*Ber.*, 1889, **22**, 1156) found that hydrastinine gave a benzoyl derivative in which the tetrahydropyridine ring had presumably been opened, and on oxidation gave what was probably *N*-benzoyl-β-(4 : 5-methylenedioxy-2-carboxyphenyl)ethylmethylamine (IV). Attempts to benzoylate substance (III), however, resulted in the conversion of the benzoyl chloride into benzoic anhydride, the ψ-base acting merely as a catalyst.



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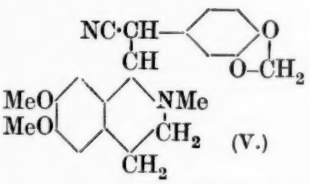


(V.)

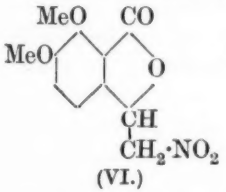
In the proposed synthesis of cryptopine, the substance (I) was to have been esterified and condensed, in presence of sodium ethoxide, with homopiperonylonitrile, $(CH_2O_2)C_6H_3·CH_2·CN$, or a derivative of it with a substituent in the ortho-position to the $-CH_2·CN$ group. Attempts to prepare this nitrile from homopiperonal by Semmler and Bartelt's method (*Ber.*, 1908, **41**, 2751) gave minute yields, valueless for synthetic purposes. Interaction of piperonyl bromide

and alcoholic potassium cyanide led to *piperonyl ethyl ether*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$. The nitrile was most conveniently prepared by condensing piperonal with hippuric acid, hydrolysing the resulting so-called azlactone to piperonylpyruvic acid (Kropp and Decker, *Ber.*, 1909, **42**, 1188; compare Buck and Perkin, J., 1924, **125**, 1680), and treating the *oxime* of this with acetic anhydride, whereby the nitrile was produced by loss of carbon dioxide and water.

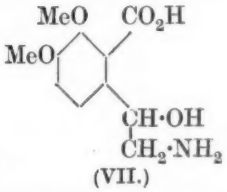
Homopiperonylonitrile condenses with the ψ-base (III) in warm alcohol. The product, 6 : 7-*dimethoxy*-1(3′ : 4′-*methylenedioxy*-ω-*cyanobenzyl*)-2-*methyltetrahydroisoquinoline* (V) does not give a benzoyl derivative under any of the normal conditions of benzoylation, and after several unsuccessful attempts to open the ring between the 1-carbon atom and the nitrogen, this line of attack was abandoned.

The direct synthesis of the required amino-acid (I) from *m*-opianic acid was next tried. The only suitable method for preparing *m*-opianic acid in the quantities required for synthetic work is that of Fargher and Perkin (J., 1921, **119**, 1724), which makes use of creosole. Only a small quantity of this being available, a preliminary investigation was made with the more readily accessible opianic acid (Edwards, Perkin, and Stoyle, J., 1925, **127**, 197), three methods of converting it into the required type of substance being examined.

Opianic acid condensed with nitromethane to give a substance (VI) which on reduction yielded the *lactone* of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylamine hydrochloride* (VIII). The base



(VI.)



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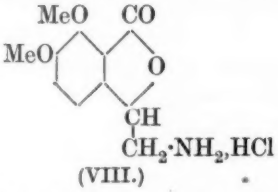
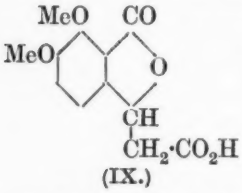


(VIII.)

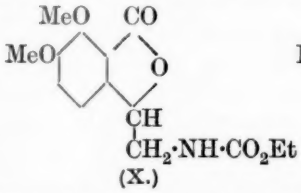
corresponding to this was formed on treatment with one molecular proportion of cold alkali, whilst hot alkali gave the amino-acid itself (VII). The latter, on being heated alone or in tetralin, lost water and ammonia, leaving a nitrogen-free, resinous substance, and treatment with reagents which attack the amino-group resulted in the formation of derivatives of the amino-lactone (VIII). The poor yields obtained by this method are probably due to the decomposition of the condensation product by the acid reducing agents.

Opianic acid condensed with malonic acid to give meconine-acetic acid (IX) (Liebermann, *Ber.*, 1886, **19**, 2290), the amide of

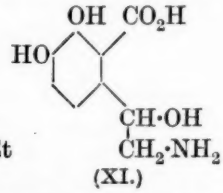
which in the Hofmann reaction, when carried out under the conditions used by Decker (*Annalen*, 1913, **395**, 291) in the preparation of substituted phenylethylamines from phenylpropionamides, gave about a 30% yield of the amino-acid (VII). The alternative Curtius reaction proceeded quite smoothly as far as the *carbamate* (X), which proved unexpectedly stable towards acid hydrolysing reagents, boiling concentrated hydrochloric acid leaving it unchanged. When the hydrolysis mixture was heated in a sealed tube at 140—150°, hydrolysis of the carbamate was accompanied by that of the two methoxy-groups, the product being β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dihydroxyphenyl*)*ethylamine* (XI). This is a typical catechol derivative, giving an intense green coloration with ferric chloride and oxidising rapidly in air. It is similar in properties to the amino-acid already described. In the cold, sodium hydroxide



(IX.)



(X.)

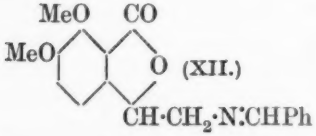


(XI.)

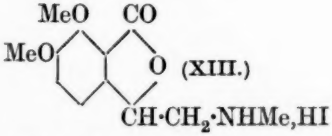
merely opened the lactone ring of the carbamate (X), but a boiling solution removed the carbethoxy-group as well. The resulting solution on careful neutralisation slowly deposited the amino-acid (VII).

Of the three methods discussed above, the Curtius reaction gives the best yield, *viz.*, 40% of the theoretical, calculated on the quantity of opianic acid taken.

The amino-acid (VII) was converted into the benzylidene compound (XII), the methiodide of which, on hydrolysis, yielded the lactone of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylmethylamine hydriodide* (XIII). On opening the lactone ring, the corresponding amino-acid was formed; it at once passed into its lactone on treatment with mineral acids or with reagents which attack the amino-group.



(XII.)

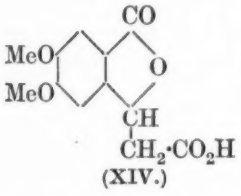


(XIII.)

Benzenesulphonyl derivatives of the amino-acids may be prepared by treating the sodium salts with benzenesulphonyl chloride and caustic soda. The dimethylation of the product and the condensation of the ester group with the reactive methylene group in

such substances as phenylacetonitrile and phenylacetic ester will be dealt with in a later paper.

m-Opianic acid condensed best with malonic acid when dissolved in pyridine containing a trace of piperidine. The product, m-*meconineacetic acid* (XIV), was converted by the modification of the Curtius reaction already described into β-hydroxy-β-(4 : 5-dimethoxy-2-carboxyphenyl)ethylamine (XV). This was methylated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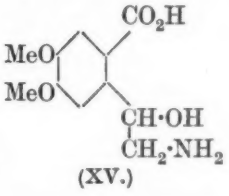
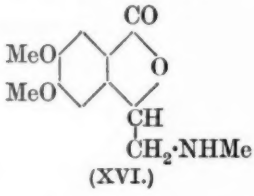

(XV.)


(XVI.)

in the form of its benzylidene derivative, and the final product (derived from its lactone XVI) was precisely similar in properties to the amino-acids already described.

The quantity of creosole available proved sufficient for the production of only about 5 grams of the amino-acid. The production of this substance in quantity from *m*-meconine by another method is being investigated.

Experimental.

r-*Laudanosine* (*N*-methyltetrahydropapaverine) was obtained in almost quantitative yield by reducing papaverine methosulphate with zinc and alcoholic sulphuric acid. The yield obtained in Pictet and Finkelstein's process (*Ber.*, 1900, **332**, 346), *viz.*, reduction of the methiodide with tin and concentrated hydrochloric acid, is about 50%.

The solid obtained by heating papaverine (50 g.) and methyl sulphate (16 c.c.) on the water-bath for 30 minutes was dissolved in boiling water (200 c.c.), mixed with alcoholic sulphuric acid (25 c.c. of 30% solution), and the whole heated on the water-bath while zinc dust and alcoholic sulphuric acid were added alternately so that hydrogen was gently evolved. After 2½ hours, the boiling solution was filtered, the zinc washed thoroughly with boiling alcohol, and the hot solution added slowly to ammonia (350 c.c.; *d* 0·880) mixed with powdered ice. The product separated slowly as a voluminous mass of needles, and after one recrystallisation from dilute alcohol was pure, m. p. 115°.

Piperonyl Ethyl Ether.—An alcoholic solution of piperonyl bromide (Orr, Robinson, and Williams, J., 1917, **111**, 950; Robinson and Robinson, J., 1914, **105**, 1463) and excess of sodium ethoxide was warmed on the water-bath for 10 minutes and poured

into water. The *ether*, which was extracted with ether, was a pleasant-smelling oil, b. p. 130—133°/13 mm. (Found: C, 66·4; H, 6·4. $C_{12}H_{10}O_3$ requires C, 66·7; H, 6·7%).

Oxime of Piperonylpyruvic Acid.—A solution of piperonylpyruvic acid and hydroxylamine hydrochloride (1½ equivs.) in 8% aqueous sodium hydroxide (3 equivs.) was heated on the water-bath for 1 hour. According as it was acidified with acetic acid or hydrochloric acid the solution deposited the insoluble sodium salt of the oxime or the *oxime* itself. The white, flocculent precipitate of the latter was separated after 12 hours; it crystallised from alcohol in colourless needles, m. p. 174—175° (Found: N, 6·1. $C_{10}H_9O_5N$ requires N, 6·3%).

Homopiperonylonitrile.—The preceding oxime was gently warmed with acetic anhydride (4 parts); the reaction, at first slow, ultimately became very violent, and water-cooling was usually necessary. The product was distilled in a vacuum; the nitrile then passed over as a golden-yellow liquid, b. p. 160°/10 mm. It quickly solidified on treatment with absolute alcohol, and on recrystallisation from dilute alcohol separated in nearly colourless needles, m. p. 49° (Medinger, *Monatsh.*, 1906, **27**, 237, gives m. p. 42°) (Found: C, 67·2; H, 4·4; N, 8·5. Calc., C, 67·1; H, 4·3; N, 8·7%).

6 : 7-*Dimethoxy*-1-(3′ : 4′-*methylenedioxy*-ω-*cyanobenzyl*)-2-*methyltetrahydroisoquinoline* (V).—1-Hydroxy-6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline (III) (Pyman, *loc. cit.*) was dissolved together with homopiperonylonitrile (1 mol.) in hot alcohol. The condensation product separated from the cooled solution in needles, which melted at 171° to a dark red liquid (Found: C, 68·8; H, 6·0. $C_{21}H_{22}O_4N_2$ requires C, 68·8; H, 6·0%). It is completely decomposed when boiled with caustic soda, and is a moderately strong base. On treatment with formaldehyde, methylal or methylene odide, high-melting bases are formed. Since these substances were obviously not of the tetrahydro*epi*berberine type, they were not further investigated.

Synthesis of β-*Hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylmethylamine.*

Reduction of Meconine-nitromethane.—Meconine-nitromethane (15 g.) was dissolved with cooling in concentrated hydrochloric acid (200 c.c.) containing stannous chloride (42 g.); much heat was generated, and the liquid soon began to deposit a yellow tin salt. After an hour, this was filtered off, washed with hydrochloric acid, dissolved in boiling water, the tin removed with hydrogen sulphide, and the filtrate evaporated to small bulk. The hydrochloride thus obtained crystallised from dilute alcohol in colourless needles, m. p.

248°, and was the *lactone* of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylamine hydrochloride* (VIII) (Found : C, 51·4; H, 5·3. $C_{11}H_{13}O_4N$,HCl requires C, 51·0; H, 5·4%).

The *picrate* of the base separated slowly in golden-yellow needles, m. p. 202—204° (decomp.), when a hot solution of the hydrochloride and picric acid in water was cooled.

Meconineacetamide.—Meconineacetic acid (Liebermann, *loc. cit.*) (40 g.) was boiled for ½ hour with thionyl chloride (130 c.c.), the acid chloride crystallising in fine needles. The excess of thionyl chloride was distilled off on a water-bath; the crystalline residue, after being washed with dry ether and dried in a steam-oven, melted at 158—159° and was sufficiently pure for immediate use.

The finely-powdered acid chloride was added slowly to aqueous ammonia (*d* 0·880; 250 c.c.) containing ice. After 1 hour, the white, amorphous product was washed with cold alkali and ether and crystallised from glacial acetic acid; it then separated in colourless masses of prisms, m. p. 223—224°. It was quite insoluble in cold alkalis, but dissolved readily, on warming, with evolution of ammonia. The latter treatment also opened the lactone ring, but all attempts to effect this change without attacking the amino-group were unsuccessful (Found : C, 57·5; H, 5·2; N, 5·6. $C_{12}H_{13}O_5N$ requires C, 57·3; H, 5·1; N, 5·6%).

The esters of meconineacetic acid may be prepared by cooling a solution of the acid chloride in the minimum amount of the hot alcohol. The methyl ester was thus obtained in colourless hexahedra, m. p. 124°, identical with that obtained by Liebermann (*loc. cit.*) by direct esterification.

Action of Sodium Hypochlorite upon the Acid Amide.—The finely-powdered acid amide, suspended in water at 60°, was shaken with exactly 1·2 mols. of sodium hypochlorite. When the solid had dissolved, the liquid was made very strongly alkaline with caustic soda, the temperature allowed to rise slowly to 85°, and, after ½ hour, the solution was cooled and made just perceptibly acid to litmus by addition of acetic acid. β-*Hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylamine* (VII) separated slowly as a microcrystalline powder, m. p. 224°. It was insoluble in all non-hydroxylic organic solvents, and very sparingly soluble in boiling alcohol or water. A solution of the crude substance in hot ammonia was filtered from insoluble impurities and boiled; as the ammonia evaporated, the amino-acid slowly separated in colourless needles, m. p. 225°. The substance is more soluble in hot solutions of such inorganic salts as copper sulphate and silver nitrate than in water, but separates from them unchanged (Found : C, 54·5; H, 6·1. $C_{11}H_{14}O_5$ requires C, 54·8; H, 6·2%).

Treatment of the amino-acid with hydrochloric acid at once converted it into the hydrochloride of the lactone (VIII), identical with the substance obtained from meconine-nitromethane. When the solid hydrochloride was treated with the theoretical quantity of 30% ice-cold caustic soda solution, it was converted into the lactone base, which is a colourless, fishy-smelling oil, very soluble in water but insoluble in non-hydroxylic solvents. The lactone ring was opened by warming with caustic soda solution for a few minutes, and the amino-acid was precipitated on making the solution just perceptibly acid to litmus with acetic acid.

The amino-acid was boiled with acetic anhydride (3 parts) for 10 minutes and the solution was then refluxed for ½ hour with its own bulk of absolute alcohol, evaporated to one-fourth its volume, and diluted with dry ether. The *acetyl* derivative of the lactone base separated in colourless needles, which crystallised from xylene in star-shaped clusters, m. p. 155° (Found: C, 58·6; H, 5·7. $C_{13}H_{15}O_5N$ requires C, 58·8; H, 5·7%).

Preparation of the Amino-acid (VII) *by means of the Curtius Reaction.*—Meconineacetyl chloride (20 g.) was added slowly to hydrazine hydrate (20 g.) cooled in ice. The resulting thick paste of meconineacetylhydrazide was thoroughly ground and, after 12 hours, dissolved in 8% hydrochloric acid (200 c.c.). A bulky, amorphous precipitate slowly separated. This was filtered off, and the filtrate cooled in ice and treated slowly with sodium nitrite (34 g. in the minimum of water). *Meconineacetyl azide* separated as a white solid (14 g.) and was washed with dry ether and dried in a vacuum desiccator. A small portion recrystallised from dry chloroform separated in colourless needles. It was comparatively stable, losing nitrogen only when heated at its melting point, 94°, for a short time (Found: N, 14·7. $C_{12}H_{11}O_5N_3$ requires N, 15·1%).

When the crude azide was boiled for ½ hour with absolute alcohol (2 parts), a violent evolution of nitrogen took place; the solution on cooling deposited crystals of the *lactone* of *ethyl* β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylcarbamate* (X). It crystallised from methyl alcohol in colourless cubes, m. p. 131° (Found: C, 56·9; H, 5·8; N, 4·7. $C_{14}H_{17}O_6N$ requires C, 56·9; H, 5·8; N, 4·7%).

This carbamate was heated with concentrated hydrochloric acid (6 parts) in a sealed tube at 150° for 3 hours. The insoluble liquid thus produced was mainly methyl chloride. The aqueous liquid in the tube was boiled, filtered hot, and allowed to cool, β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dihydroxyphenyl*)*ethylamine hydrochloride* being thus obtained in colourless needles, m. p. 262—265°. On treating

this salt with ammonium carbonate, the *amino-acid* (XI) was obtained in colourless needles, m. p. 138—140° (Found : C, 50·3; H, 5·3. $C_{19}H_{12}O_4N$ requires C, 50·7; H, 4·8%). The amino-acid dissolved readily in warm dilute acids or alkalis, but not in alkali carbonates. It did not form a lactone under the conditions obtaining in the case of the dimethoxy-compound.

The carbamate (12 g.) was dissolved in 15% sodium hydroxide solution (50 c.c.) by heating on the water-bath for ½ hour. After boiling for 5 minutes, the solution was cooled, filtered, and faintly acidified (litmus) with acetic acid. After 12 hours, the amino-acid (VII) separated as a microcrystalline powder, m. p. 224°. The yield was 7 g. from 20 g. of meconineacetic acid, *i.e.*, 40%.

From the solution obtained by boiling the amino-acid (30 g.) and benzaldehyde (60 c.c.) for 20 minutes the greater part of the excess of benzaldehyde was removed in a vacuum. The residue was mixed with boiling methyl alcohol (220 c.c.); from the filtered cooled solution the *benzylidene* derivative of the lactone base (XII) separated in slightly cream-tinged plates, m. p. 125° (Found : C, 69·2; H, 5·5. $C_{18}H_{17}O_4N$ requires C, 69·4; H, 5·5%).

The benzylidene compound was heated for 2 hours with its own weight of methyl iodide in a sealed tube at 100°. The orange liquid thus formed set, on cooling, to a mass of yellow needles, which was at once washed with carefully dried benzene and dried in a vacuum desiccator. The *methiodide* thus obtained melted at 180°. It decomposed rapidly in the air with liberation of benzaldehyde. Hydrolysis was best carried out by boiling for a short time with four parts of 95% ethyl alcohol; the filtered solution, on cooling, deposited the *lactone* of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*) *ethylmethylamine hydriodide* (XIII) in colourless prisms, m. p. 220—222°. The *hydrochloride*, prepared by boiling the hydriodide in chloroform solution with phosphorus pentachloride for 10 minutes, separated from alcohol in felted needles, m. p. 233°. The *nitroso*-compound separated in colourless needles, m. p. 108°, when a warm aqueous solution of the hydrochloride was dropped slowly into an ice-cold solution of excess of sodium nitrite (Found : C, 54·0; H, 5·2; N, 10·7. $C_{12}H_{14}O_5N_2$ requires C, 54·1; H, 5·2; N, 10·5%). From the solution obtained by shaking the hydrochloride and benzoyl chloride (1 mol.) with aqueous sodium hydroxide (2 mols.) the *benzoyl* derivative separated slowly; the large amount remaining in solution was extracted with ether. The product crystallised from a little methyl alcohol in rhombs, m. p. 106°. This substance is insoluble in cold caustic soda solution, but dissolves readily on warming (Found : C, 67·2; H, 5·7. $C_{19}H_{19}O_5N$ requires C, 66·9; H, 5·5).

β-*Hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylmethylamine* (VII with NHMe in place of NH_2) was obtained by heating a salt of the amino-lactone on the water-bath with a slight excess of caustic soda solution for ½ hour and just acidifying the cooled solution with acetic acid. It crystallised slowly from water in colourless plates, m. p. 190—192° (Found : C, 56·2; H, 6·8. $C_{12}H_{17}O_5N$ requires C, 56·5; H, 6·6%).

β-*Hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylmethylamine* (XV *with* NHMe *in place of* NH_2).

m-*Meconineacetic Acid.*—*m*-Opianic acid (28 g.), malonic acid (35 g.), piperidine (30 drops), and pyridine (100 c.c.) were heated on a water-bath for 6 hours. After boiling for a few minutes, the mixture was cooled and poured into 16% hydrochloric acid (300 c.c.); the product, which separated slowly in clusters of needles, crystallised well from a little glacial acetic acid in colourless needles, m. p. 230—231° (Found : C, 56·8; H, 5·0. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8%).

m-*Meconineacetyl Chloride.*—*m*-Meconineacetic acid was boiled for ½ hour with twice its weight of thionyl chloride, the excess of solvent was removed in a vacuum, and the yellow, syrupy product was made to crystallise by treatment with dry ether. It separated from dry xylene in colourless prisms, m. p. 103—104°.

m-*Meconineacetamide* was prepared in exactly the same way as meconineacetamide. It separated from much alcohol in clusters of needles, m. p. 240—241° (Found : N, 5·6. $C_{12}H_{13}O_5N$ requires N, 5·6%).

Ethyl m-*meconineacetate* was produced when the acid chloride was dissolved in a little hot ethyl alcohol, and the product allowed to cool. It separated in fine needles, m. p. 133°. The same substance was obtained by direct esterification (Found : C, 59·8; H, 5·8. $C_{14}H_{16}O_6$ requires C, 60·0; H, 5·8%). The *methyl* ester separated from methyl alcohol in colourless plates, m. p. 129°.

m-Meconineacetic acid was converted by the method already described into m-*meconineacetyl azide*. This separated as a gummy substance which crystallised from chloroform in clusters of needles, m. p. 100° with evolution of nitrogen (Found : N, 14·8. $C_{12}H_{11}O_5N_3$ requires N, 15·1%). Treatment with alcohol converted this into the *lactone* of *ethyl* β-*hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylcarbamate*, which separated in glistening plates with a pale brown tinge, m. p. 177—178° (Found : C, 56·9; H, 5·8; N, 4·7. $C_{14}H_{17}O_6N$ requires C, 56·8; H, 5·6; N, 5·0%). Hydrolysis of this with four times its weight of 12% aqueous caustic soda gave a clear solution which, on being cooled and just acidified with acetic acid, deposited β-*hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylamine*

(XV) in fine, hexagonal prisms, m. p. 204—205° (Found : C, 54·5; H, 6·0. $C_{11}H_{14}O_5N$ requires C, 54·8; H, 6·2%). The acid readily formed a *benzylidene* compound in the manner described above, which crystallised from methyl alcohol in colourless needles, m. p. 146° (Found : C, 69·1; H, 5·7. $C_{18}H_{17}O_4$ requires C, 69·4; H, 5·5%). When quite dry, the latter added on methyl iodide in the manner already described, and the *methiodide* was hydrolysed on treatment with hot dilute alcohol to the *lactone* of β-*hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylmethylamine* (XVI), which crystallised from ethyl alcohol in colourless prisms, m. p. 230—231°. Treatment of this with caustic soda solution opened the lactone ring and produced the amino-acid, which was purified by boiling its solution in ammonia until no more crystals separated. It was thus obtained in needles, m. p. 199—204° (decomp.) (Found : C, 56·9; H, 6·8. $C_{12}H_{17}O_5N$ requires C, 56·5; H, 6·6%).

The author wishes to thank Professor W. H. Perkin, F.R.S., for many helpful suggestions, and the Advisory Council of the Department of Scientific and Industrial Research for a grant which enabled him to carry out the greater part of this investigation.

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CIV.—*The Electrometric Titration of Halides.*

By WALTER CLARK.

THE object of the experiments to be described was to examine the possibility of applying electrometric methods to the analysis of mixtures of soluble halides and of mixed silver halides, in particular where one halide is present in small proportion—less than 1%—in the other.

The estimation of a single soluble halide by titration with silver nitrate, or conversely of silver ions by titration with a halide solution, can be accurately and simply carried out electrometrically (compare Behrend, *Z. physikal. Chem.*, 1893, **11**, 466; Dutoit and von Weise, *J. Chim. Phys.*, 1911, **9**, 578, 608, 630). For this purpose several different methods have been devised. Certain of these have been summarised by Kolthoff (*Chem. Weekblad*, 1920, **17**, 659), Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504), and Müller (" Elektrometrische Massanalyse," 2nd edn, 1923).

The most exact method of titration is that in which the titration beaker containing the halide solution and a silver electrode is

connected with a normal electrode, and the *E.M.F.* of the combination is measured after each addition of silver nitrate, the end-point of the titration being taken as the point of maximum rate of change of *E.M.F.* with silver ion added.

In an arrangement due to Pinkhof (*Diss.*, Amsterdam, 1919; *Chem. Weekblad*, 1919, **16**, 1163; *Pharm. Weekblad*, 1919, **56**, 1218) the normal electrode is replaced by a compensation electrode whose potential is equal to that of the titration system at the end-point. With this method a different compensation electrode would be required for each halide titrated, and in the titration of mixed halides the electrode would have to be changed during the course of the titration.

A variation of Pinkhof's method has been used extensively by Treadwell (*Helv. Chim. Acta*, 1919, **2**, 672, 680), and a modification for use with 5 c.c. of solution to be titrated, has been described by Garner and Waters (*J. Soc. Chem. Ind.*, 1922, **41**, 337T).

A further method of titration consists in the use of " bimetallic electrode systems," introduced by Willard and Fenwick (*J. Amer. Chem. Soc.*, 1922, **44**, 2504, 2516; 1923, **45**, 623), and suggested also by Müller (*Z. Elektrochem.*, 1924, **30**, 420) and Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1343). This method has been applied also to acid-alkali titrations by van der Meulen and Wilcoxen (*Ind. Eng. Chem.*, 1923, **15**, 62) and by Brünnich (*ibid.*, 1925, **17**, 631).

Another method of titrating soluble halides has recently been described and is worthy of note. In the " differential titration " method of Cox (*J. Amer. Chem. Soc.*, 1925, **47**, 2138) the halide solution is divided equally between two beakers joined by an ammonium nitrate bridge and each containing a silver electrode connected with the potentiometer. Both solutions are titrated simultaneously with silver nitrate, one being kept slightly in advance of the other, and the potential is read after each addition of silver. The titration curve obtained is the first derivative of the normal titration curve, and its maximum is the end-point.

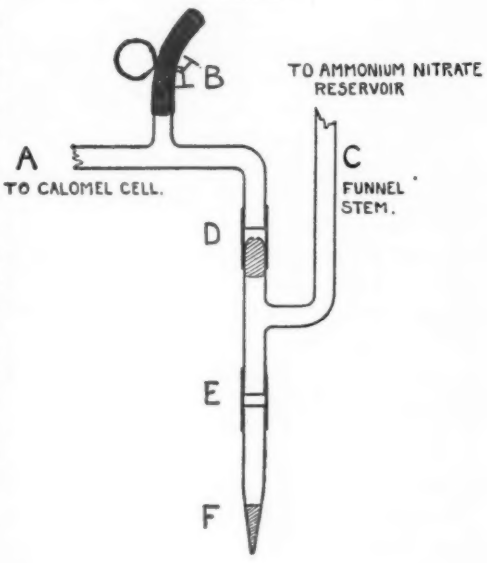
In the investigation to be described the first method of titration was used, *i.e.*, that in which the solution to be titrated contained a silver electrode and was united with a calomel cell, the *E.M.F.* of the combination being measured by means of a potentiometer after each addition of silver nitrate. This method was used because it is quite straightforward and can be used for the titration of mixed halides without changing the electrode or the constant half-cell. It was examined first with a view to its utility for the accurate yet simple estimation of mixtures of two or three alkali halides by direct titration with silver nitrate solution, and then for estimating

mixtures of silver halides. In a few instances, other methods of titration were tested.

EXPERIMENTAL.

The calomel cell employed was of the saturated potassium chloride type. This was united with the halogen solution to be titrated by a saturated ammonium nitrate bridge in such a way as to prevent diffusion of chloride from the cell into the titration beaker, and to prevent loss of halide from the solution to be titrated by displacement with the specifically heavier ammonium nitrate solution. The arrangement is shown in Fig. 1.

FIG. 1.



A is a continuation of the side arm of the calomel cell. In the cell itself a wad of glass wool is placed over the surface of the calomel to prevent its disturbance when flushing out with fresh potassium chloride solution. At B is a side tube with clip to allow of the easy removal of air or old potassium chloride from the tube A D when filling it or when renewing the potassium chloride solution. An ordinary separating funnel is used as a reservoir for the saturated ammonium nitrate. The end of its stem, C, is bent at right angles and a T-piece, D E, is joined on so that D E is parallel to the stem of the funnel. At the upper end, D, the T-piece is constricted, leaving an orifice about 1 mm. in diameter. This partially closed end D is packed tightly to a depth of 1 cm. with filter-paper, previously moistened with ammonium nitrate solution. The lower end, E, of the T-piece is joined by rubber tubing to a drawn-out tube, F, which is immersed in the solution to be titrated. The tapered end of F is also packed tightly to a depth of 1 cm. with a wad of filter-paper moistened with ammonium nitrate solution. The calomel cell is connected with the ammonium nitrate bridge at D by a short piece of rubber tubing.

By means of the side tube and clip at B it is possible to flush out the calomel cell with fresh potassium chloride solution without disturbing the ammonium nitrate bridge. By removing the tube F the nitrate bridge can be flushed out from the reservoir above without disturbing the calomel cell. It is not necessary to change the wad of filter-paper at D often, but the tube F should be changed frequently.

Observations showed that in the course of several hours no chloride reached the titration solution from the calomel cell, and no loss of chloride from the titration solution into the bridge could be detected.

The solution to be titrated was stirred by a motor-driven stirrer at 200 revolutions per minute.

For the silver electrode, No. 20 gauge fine silver wire, provided by Messrs. Johnson Matthey, was used. For the best results it has to be specially treated, as described later. A Cambridge and Paul potentiometer, giving readings to 0·5 millivolt, was used for measuring electromotive forces.

The method of titration was to run standard silver nitrate solution *drop by drop* into the stirred solution of halide, the *E.M.F.* being read after each addition of 1 c.c. When the *E.M.F.* began to rise more rapidly, only 0·1 c.c. of silver nitrate solution was added. When great accuracy was desired, or when only small amounts of halide were being titrated, silver nitrate was added from a microburette, or more generally, a $N/100$- or $N/1000$-solution was used, in the neighbourhood of the end-point.

In most cases, a certain time was necessary for establishment of equilibrium of *E.M.F.* in the immediate neighbourhood of the end-point. This will be considered in the course of the description of the titration. The end-point of the titration was obtained either by plotting the titration curve of c.c. of silver nitrate added against *E.M.F.*, and determining its point of inflexion or the mid-point of the maximum slope, or, more readily, by plotting the first derivative of the titration curve, *i.e.*, dE/dV, against V, where E is the *E.M.F.* corresponding to a volume V of silver nitrate added (compare, for example, Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1341). Each of these methods of determining the end-point was used as occasion demanded, for in certain forms of titration curve one method is preferable to another.

Titration of Solutions of Soluble Halides.

Preparation of Pure Materials.—Silver nitrate solutions of $N/10$, $N/100$ and $N/1000$ strength were made up from Johnson's "pure

triple crystallised silver nitrate," which is specially prepared for the manufacture of photographic emulsions.

Potassium chloride, free from other halides, was available as a commercial product, and approximately $N/10$-solutions were prepared.

No commercial sample of bromide or iodide free from chloride was available. Many samples of ammonium and potassium bromide, and of ammonium, barium, cadmium, and potassium iodide were examined quantitatively for chlorides. The proportion present varied with different samples from 0·2% to about 5%, and with a number of samples of any one salt from any one manufacturer, wide variations were found. Potassium bromide was the worst offender in this respect.

Preparation of Pure Bromide.—A sample of potassium bromide, free from chloride and bromate, was prepared by heating once-recrystallised potassium bromate in a silica basin, extracting the fused salt with water, and evaporating the solution to dryness.

Ammonium bromide free from chloride was prepared from purified ammonia and bromine. A sample of commercial ammonia solution, labelled " sp. gr. 0·880, extra pure," contained a trace of chloride which was removed by boiling off the ammonia gas and reabsorbing it in distilled water.*

For the preparation of pure bromine, the purest commercial bromine, which contained some chlorine, was used. 100 G. were shaken with 50 c.c. of concentrated potassium bromide solution, and then distilled off on a water-bath at 70—90°. The distilling apparatus was made entirely of glass, and the receiver was cooled in ice.

The yield of 70 g. of bromine was well shaken with 5 c.c. of N-caustic soda solution and distilled again in the same apparatus (compare Scott, J., 1913, **103**, 847; Baxter, *Proc. Amer. Acad. Arts Sci.*, 1906, **42**, 201).

Ammonium bromide was made by adding the bromine drop by drop, shaking after each addition, to freshly-distilled ammonia contained in an ice-cooled flask until there was only a slight excess of ammonia. This excess was boiled off and the solution evaporated to dryness. The product was free from chloride and bromate.

Preparation of Pure Iodide.—Baxter (*Proc. Amer. Acad. Arts Sci.*, 1903, **39**, 249; 1904, **40**, 419; 1906, **42**, 201) has described the conditions for the preparation of pure bromine and iodine. The method he adopted in the case of iodine did not give successful results in the author's hands. Also attempts were made to prepare

* Addition of a few drops of silver nitrate solution to the ammonia before distillation ensures the freedom of the final product from chloride.

pure ammonium iodide somewhat on the lines described by Baxter, but without success. It was found impossible to remove the last traces of chloride; under the conditions employed, between 0·1% and 0·2% chloride remained.

Some of the earlier experiments on electrometric titrations, to be described later, suggested a method for the preparation of iodide free from chloride which was very satisfactory and simple. It is briefly as follows:

Ordinary commercial potassium iodide is dissolved in a 5% solution of chloride-free barium nitrate (sodium nitrate, ammonium nitrate or sodium acetate may also be used) and silver nitrate solution is run in slowly drop by drop, with vigorous stirring, a marked excess of soluble halide, however, being left finally. This excess must be larger than the equivalent of chloride present. Silver equivalent to 90% of the iodide was used in the actual preparations. Under these conditions, the precipitate consists entirely of silver iodide and all the chloride remains in solution. The silver iodide precipitate is removed and washed several times with water. It is then suspended in water, stirred vigorously, and reduced with hydroxylamine sulphate * and chloride-free caustic soda prepared from metallic sodium by the action of water vapour. This gives a precipitate of spongy silver, and a solution of sodium iodide, hydroxylamine, sodium hydroxide, and sodium sulphate. The liquid is filtered, evaporated to dryness, the residue is heated at about 200° to destroy the excess of hydroxylamine,† and extracted with water, and the solution neutralised with sulphuric acid. The solution of sodium iodide and sodium sulphate obtained in this way was suitable for the purpose of electrometric titration; in fact, the presence of sodium sulphate was found to be beneficial to the titration. The solutions obtained were absolutely free from chloride.

If it is desired to have pure iodide, free from sodium sulphate, the solution can be treated with permanganate, and the iodine distilled off and converted into hydriodic acid with hydrogen sulphide gas according to the method of Baxter (*loc. cit.*).

If the product still contains chloride, the iodide–sulphate solution can be again partly precipitated as silver iodide, followed by reduction as described, but in no case has more than one precipitation and reduction been found necessary.

Stock solutions of bromide and iodide of practically $N/10$-strength were prepared, and standardised against the stock $N/10$-silver nitrate solution, by the dye-indicator method of Fajans

* This can be obtained commercially quite free from chloride.

† Alternatively, an excess of silver iodide is used so that there is no excess of hydroxylamine.

and Hassel (*Z. Elektrochem.*, 1923, **29**, 495; *Kolloid Z.*, 1924, **34**, 304), fluorescein being used as indicator. The stock chloride solution was standardised by the normal titration method, with chromate as indicator.

In the titration of silver ions with halide ions, with fluorescein as indicator, it is essential to define the conditions rather closely, otherwise the true end-point is difficult to determine. It is necessary to titrate in very dilute solution, with a low concentration of dye. For example, in the titration of $N/10$-silver nitrate with $N/10$-potassium bromide it was found best to dilute 10 c.c. of the silver nitrate to about 200 c.c. with water, and use 5 drops of a 1 : 2000 solution of fluorescein as indicator. In these conditions, the silver halide does not coagulate in the neighbourhood of the end-point, and the change from rose colour to yellowish-green is sharp and readily located.

Electrometric Titration of Halides.

The solutions of soluble halides were titrated electrometrically with a standard silver nitrate solution, and the results agreed identically with those obtained by the ordinary titrations. For any further stock solutions prepared, standardisation was therefore carried out by the electrometric method.

In the titration of the single halide solutions with silver nitrate, the magnitude of the potential jumps about the end-point was roughly : for chloride, 180 mv. ; for bromide, 350 mv. ; for iodide, 500 mv., being bigger the lower the solubility of the corresponding silver salt.

The procedure in titration was to dilute the volume of halide taken to 50 c.c. in some cases, or to 150 c.c. in other cases, with water or any required solution, and then to titrate with the $N/10$-silver nitrate.

In the titration of bromide or iodide, no anomalies were observed which could be ascribed to the nature of the silver electrode employed. In the case of chlorides, however, certain peculiarities were observed which were shown to be dependent on the electrode surface.

Effects Due to the Electrode.

The first electrodes used were cleaned by scraping with emery cloth or a knife blade. In the titration of chlorides, the addition of the first drop of silver nitrate resulted in a sudden rise in potential. This jump was by no means constant, being about 40—50 mv. in certain cases, and less than 10 mv. in others. With a higher concentration of chloride, a bigger jump was sometimes observed, and its magnitude was dependent to some extent on the presence of

neutral salts. Carrying out the titration in red light did not improve matters. The jump was not due to the presence of a trace of bromide or iodide in the chloride, since its magnitude was variable for the same amount of chloride used, but was due to some peculiarity of the silver electrode, since it varied with the nature of the silver surface.

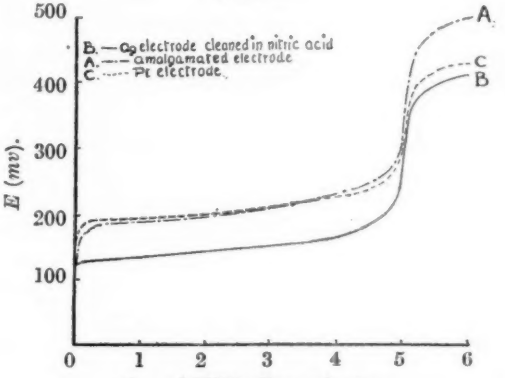
To avoid any confusion in the event of the possibility of the presence of a trace of iodide or bromide in the chloride, the conditions for obtaining an electrode which did not give the initial jump were studied. A long series of experiments showed that plating the electrode from a potassium argentocyanide solution does not give a reproducible electrode which comes into equilibrium with the chloride immediately. Various other methods of treatment showed that if the electrode was first cleaned with emery cloth and then immersed, until gassing freely, in a solution of nitric acid (1 : 1) to which a little sodium nitrite had been added, it assumed equilibrium immediately on being immersed in the chloride solution, and the potential alteration on addition of the first drop of silver nitrate was very small—never more than about 8 millivolts. Electrodes treated in this way are quite trustworthy, and were used for all the electrometric titrations.

The effect of amalgamating the electrode was next tried. Amalgamation was effected by cleaning the electrode with emery cloth and then rubbing it with mercury by means of a wad of cotton wool on a glass rod, under dilute nitric acid. With such an electrode equilibrium was established in a very short time, but the first addition of silver nitrate produced a big jump in potential, equal to 70 mv. After this, the titration curve proceeded in a normal manner, giving the same end-point as the plain silver electrode. The whole curve, however, was shifted in the direction of a higher *E.M.F.* compared with the plain silver electrode curve; *i.e.*, it was more " noble." This is shown in Fig. 2. Similar results were obtained in the titration of bromides and iodides.

This suggested a new method of titrating halides with silver nitrate by means of a bimetallic electrode system, the use of a calomel cell thus being eliminated. If two electrodes, one of amalgamated silver and the other of plain silver, are immersed in a chloride solution to be titrated, the resulting titration curve should be the difference between curves A and B in Fig. 2. This difference is practically constant until, in the neighbourhood of the end-point, a deviation occurs, giving a sharp break in the curve, after which it becomes constant again. Measurements showed that this method affords a means of determining a halide as accurately as the other methods used. The breaks at the end-point are very sharp and the magnitude

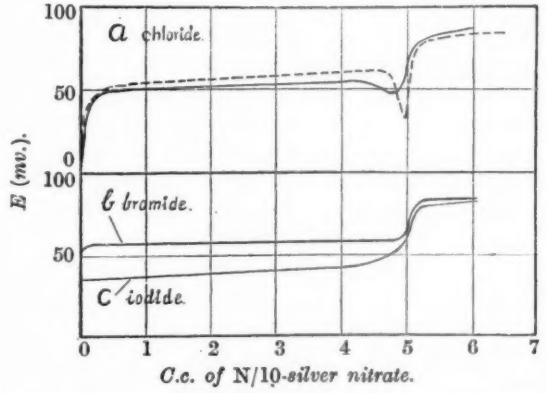
of the jumps in the case of chloride, bromide, and iodide are about 30—40 mv. Fig. 3 shows titration curves for chloride, bromide, and iodide. In the neighbourhood of the end-point, it is necessary to allow a minute or so for equilibrium to be attained after each addition of silver ions.

FIG. 2.



The dotted curve in Fig. 3 (*a*) is the curve calculated by subtracting the two curves A and B of Fig. 2. It agrees well with the curve obtained by direct titration with the bimetallic system. In the case of chloride only, a drop in the curve is observed in many cases,

FIG. 3.



before the final jump, although in some chloride titrations this drop is absent. The end-point of curves which exhibit this drop is at the point of maximum slope of the final jump. All curves obtained by this bimetallic method exhibit an initial jump on the first addition of silver ions, owing to the amalgamated electrode always

showing such a rise. The method has not yet been applied to mixtures of halides. In the titration of iodides, the curves with plain silver and with amalgamated silver were actually coincident for some distance at the end-point, and yet the bimetallic titration showed a marked jump at the end-point. Müller (*Z. Elektrochem.*, 1924, **30**, 420) appears to think that if the curves are tangential the potential should drop to zero at the end-point; but this is not necessarily so.

In many cases of normal titration with a silver wire and calomel cell, some time, often $\frac{1}{2}$ hour, is required for the attainment of equilibrium of *E.M.F.* in the immediate neighbourhood of an end-point, especially in titrations with very dilute silver nitrate. During this time, the potential rises, rapidly at first, then more slowly, and finally reaches a steady value. This change corresponds with what is equivalent to a slow increase in silver-ion concentration, and obviously is not due, therefore, to the silver ions taking a long time to react with the halide ions remaining. It appears to be due to the time taken for the silver electrode to assume equilibrium with the changed concentration of silver ion.

If an electrode which has been used for one titration of halide is not scraped clean and treated with nitric acid before being used again, the *E.M.F.* found for the new system before the addition of any silver ions is somewhat higher than when a freshly-cleaned electrode is used, and the initial potential jump is very small. The electrode seems to be " formed " in some way, during the first titration.

Good titration curves giving correct end-points are obtained if a bright platinum wire instead of a silver wire is used in conjunction with a calomel cell (compare Müller, *Z. Elektrochem.*, 1924, **30**, 420). The curve shows an initial jump of about 40 mv., and lies above the curve for the silver electrode, as shown in Fig. 2. Attempts to use a bimetallic electrode system of platinum and silver gave very poor results, which were useless in practice.

Titration of Mixed Halides.

The solubility products of the silver halides are of the order: silver chloride, 10^{-10}; silver bromide, 10^{-12}; silver iodide, 10^{-16}. Theoretically, then, if silver nitrate is added slowly to a mixture of, say, bromide and chloride in solution, precipitation of the bromide should be complete before that of the chloride begins. In practice, this does not occur; some chloride is precipitated along with the bromide before all the bromide is thrown down, and if a mixture of bromide and chloride in water is titrated electrometrically with silver nitrate, an error in the values is found.

That the individual halides cannot be separated quantitatively from a mixture of halides by addition of silver nitrate has long been known. It has been commented on by many workers, including Foerster ("Elektrochemie Wässerige Lösungen," 3rd edn, 1922, p. 165), Mellor ("Treatise on Inorganic Chemistry," Vol. III, pp. 418—419), Sheppard and Trivelli ("Silver Bromide Grain of Photographic Emulsions," 1921, pp. 42 *et seq.*), Küster (*Z. anorg. Chem.*, 1898, **19**, 81), Küster and Thiel (*ibid.*, 1900, **23**, 25), Thiel (*ibid.*, 1900, **24**, 1), and Müller ("Elektrometrische Massanalyse," 2nd edn, 1923).

The electrometric titration curve of a mixture of two or three soluble halides with silver nitrate shows a sudden break in the neighbourhood of the end-point of each halide, the iodide break occurring before the bromide break, which comes before the final chloride break. The arguments which apply to any pair of halides are obviously applicable to titration of a mixture of all three, so only pairs of halides will be considered at first. If a mixture of chloride and bromide in water, with no other additions, is titrated with silver nitrate, the bromide end-point appears too late, whilst the final break appears in its true position. This results in a correct estimate of the total halide, but a too high value for bromide and a too low value for chloride. The same applies in the case of bromide–iodide mixtures. With chloride–iodide mixtures the error is practically non-existent. It seems to be the general opinion that the end-point error is due to the formation of solid solutions as described by Küster and Thiel (*loc. cit.*), adsorption phenomena playing a preliminary rôle.

According to Dutoit and von Weisse (*J. Chim. Phys.*, 1911, **9**, 630) iodide can be accurately titrated in presence of a large excess (600 times or more) of chloride or bromide. This is true for iodide in chloride, but certainly not for iodide in bromide.

The end-point error increases in the series : chloride–iodide < bromide–iodide < chloride–bromide, being larger the less the solubility difference between the silver salts corresponding with a pair of halides. The magnitude of the error in the case of bromide–chloride and bromide–iodide mixtures is indicated by the following figures :

C.c. of halide solutions in terms of $N/10$-silver nitrate.

Theoretical.		Found.	
Chloride.	Bromide.	Chloride.	Bromide.
5·05	5·05	4·5	5·6
5·05	5·05	4·6	5·5
Bromide.	**Iodide.**	**Bromide.**	**Iodide.**
5·15	5·05	5·0	5·2
5·15	5·05	5·0	5·2

Two methods were tried for eliminating this error, namely: (1) working in very dilute solution, and (2) adding certain neutral substances to the titration solution.

The effect of dilution was examined on the titration of a bromide–iodide mixture. Diluting to 330 c.c. instead of the 50 c.c. normally employed in the titrations resulted in an increase in the error.

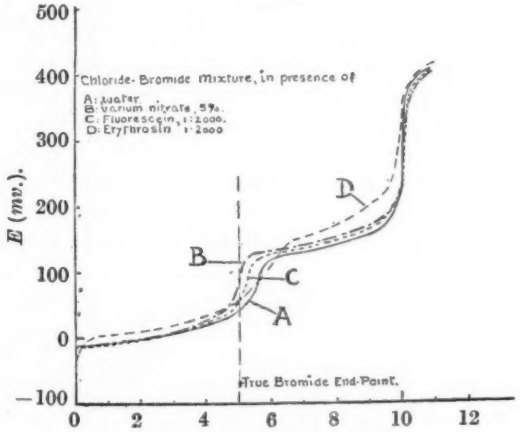
The correction of the end-point error by adding ions which are strongly adsorbed by silver halides has been studied in detail by Müller (*op. cit.*), who titrated in the presence of 5% barium nitrate solution and found that this salt prevents, or at any rate limits, the formation of solid solutions, so that the end-point error is practically eliminated. Müller writes: "The accuracy of estimation of iodide in the presence of bromide and of iodide in the presence of chloride is good in all cases in presence of 5% barium nitrate. Even the estimation of small amounts of one halide in presence of excess of the other is not affected. . . . In the estimation of bromide and chloride in the presence of one another, we must, unfortunately, reckon on an error of 1% too much bromide and correspondingly too little chloride, if equal molar concentrations of both are taken. This error increases with increasing excess of chloride, and falls off with increasing bromide excess . . . until it can be neglected when the molar concentration of bromide exceeds that of chloride by five times." Müller also mentions potassium alum in the same connexion as barium nitrate, but gives no data concerning its action. According to Foerster (*op. cit.*), in presence of barium nitrate, iodide in a ratio of iodide : bromide $> 1 : 3600$ can be estimated accurately, but bromide in chloride only when bromide : chloride $= 1 : 10$.

It appears that adsorption effects of some type are responsible for the end-point error. The exact nature of this adsorption is not quite clear, although it is probable that in the case of iodide–bromide mixtures, for example, it is adsorption of silver bromide to silver iodide which is concerned. It cannot be mere adsorption of bromide ions, because a certain amount of silver ions is involved; also it is improbable that it is adsorption of silver ions alone. It is most likely adsorption of silver bromide itself (probably colloidal), rather than the formation of a solid solution in the usually accepted sense.

Numerous measurements substantiated Müller's observations that correct end-points are obtained in presence of 5% barium nitrate solution. Lottermoser used ammonium nitrate to remove adsorbed silver from silver halides, and Fajans and his co-workers (Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495; Hassel, *Kolloid-Z.*, 1924, **34**, 304) studied the adsorption of dyes, and

adsorption replacement by dyes, on silver halides, with particular reference to a titration method for halogen and silver using fluorescein and its halogen-substitution products as indicators. These and other substances, including some which are known to be strongly adsorbed by silver halides, were investigated by the author. Since the end-point error is most marked in the case of bromide–chloride mixtures, in some cases only this mixture was investigated; in others, iodide–bromide mixtures were studied as well. The method of examination in most instances was to titrate with $N/10$-silver nitrate a mixture of 5·0 c.c. of a $N/10$-solution of each of the halides in the presence of 50 c.c. of the solution of the substance investigated.

FIG. 4.



Dyestuffs.—Erythrosin (1 in 2000), fluorescein (1 in 2000), and rose Bengal 3 (1 in 2000) gave correct end-points with the bromide–iodide mixtures. In the case of the chloride–bromide mixture, fluorescein (1 in 2000) gave a partial correction, as shown in curve C, Fig. 4. With erythrosin (1 in 2000), the final end-point for the mixture was accurate and was marked by a definite jump in potential, but the first break, representing the bromide end-point, was flattened out. In Fig. 4, curve D is a titration curve obtained in presence of erythrosin (1 in 2000). Similar results were obtained in presence of safranine (Bayer, 1 in 1000). Curve A (Fig. 4) shows the curve in presence of water alone, and curve B the correct curve, in presence of 5% barium nitrate.

Correct end-points for both chloride–bromide and bromide–iodide mixtures were obtained with 5% solutions, not only of

barium nitrate, but also of ammonium nitrate, sodium nitrate, and sodium acetate. The results with sodium acetate show that the effect is not due to the nitrate ion, and this was confirmed when it was found that *N*-sulphuric acid also gave practically complete correction.

A solution of 3·5*N*-nitric acid, with a platinum electrode, gives correct end-points with bromide–chloride mixtures, but at the final break the curve begins to rise sharply and then drops suddenly back, after which it tends to become horizontal. The system is rather insensitive and the potential readings are jerky and can be read only to the nearest 2 or 3 millivolts.

N/10-Nitric acid, with a silver electrode, gives correct end-points, and is very sensitive. For accurate work, involving a long titration time, it is conceivable that an error could be introduced owing to action of the acid on the silver electrode, but with ordinary titrations of a mixture of equivalent proportions, no error was observed. A platinum electrode is unsatisfactory with *N*/10-nitric acid.

It follows from the foregoing that although the presence of certain dyes is beneficial in the case of bromide–iodide mixtures, they are not of general value. On the other hand, barium, sodium, and ammonium nitrate, and sodium acetate in 5% solution give correct end-points with bromide–chloride and bromide–iodide mixtures for a wide variation in the proportions of the constituents of the mixtures. The presence of these salts curtails the titration time by increasing the sensitiveness of titration and lowering the time required for equilibrium potential in the region of the end-points; even for the titration of a single halide in solution their presence is beneficial. In absence of added salts, the silver halides formed in the titration remain in colloidal suspension until the final end-point is reached; if a salt is present, however, the silver halides begin to precipitate shortly after the first addition of silver nitrate.

The original object of this investigation was to study the applicability of electrometric methods to the examination of materials used in the manufacture of photographic emulsions, and to the analysis of emulsions themselves. In all the titrations made, this object was borne in mind. Consequently, in the examination of bromide–iodide mixtures, for example, low percentages of iodide in bromide were considered, rather than low percentages of bromide. A series of mixtures was studied in various circumstances to ascertain if it was easy to estimate a low percentage of one halide in the other. A limit of 0·2% of iodide in bromide and of chloride in bromide was set. The following table shows some results of measurements. The percentage composition refers to equivalents of one halide in another. The substances mentioned in the column

headed "Notes" were added to the electrolyte, 50 c.c. of a 5% solution being used in each case.

Mixture taken.	Vol. in c.c. of $N/10$-conc.	Found.	Notes.
100% Bromide.	5, 10	100% Bromide.	Same results in water, barium nitrate, sodium acetate, etc.
100% Chloride.	5, 10	100% Chloride.	
100% Iodide.	5, 10	100% Iodide.	
50% Chloride in bromide.	10	50% Chloride.	Barium nitrate, etc., *must* be present.
1·01% Chloride in bromide.	10	0·99% ,,	Barium nitrate.
0·51% ,, ,,	10	?	Sodium acetate; breaks in curve not separated.
0·50% ,, ,,	20	0·50% ,,	Barium nitrate.
0·2% ,, ,,	50	<0·25% ,, about	Sodium acetate.
0·2% ,, ,,	50	0·1% ,,	,, ,,
0·2% ,, ,,	100	0·19% ,,	,, ,,
0·2% ,, ,,	100	0·22% ,,	Barium nitrate.
50% Iodide in bromide.	10	50% Iodide.	Barium nitrate, etc.
1·6% ,, ,,	10	1·5% ,,	Barium nitrate.
0·19% ,, ,,	10	0·2% ,,	,, ,,
50% Chloride in iodide.	10	50% Chloride.	In water alone; more sensitive in presence of barium nitrate, etc.
0·2% ,, ,,	50	0·2% ,,	75 C.c. of 5% ammonium nitrate.
0·2% ,, ,,	50	0·18% ,,	75 C.c. of 5% ammonium nitrate.

The table shows that it is possible to estimate 0·2% chloride in bromide or iodide, and 0·2% iodide in bromide, with a fair degree of accuracy. The bulk of the halide was precipitated with $N/10$-silver nitrate, but for the estimation of halide present in the proportion of 1% or less, $N/100$- or $N/1000$-silver nitrate was used, an $N/10$-solution being employed only for precipitating the bulk of the halide in excess. The accuracy of estimation of a small percentage of one halide obviously depends on its absolute amount. If the absolute amount is too small, it becomes impossible to estimate the chloride present in low ratio at all, because no distinction is observed between the two breaks in the curve. Using a mixture of $N/10$-strength, it is possible to estimate 0·2% chloride in iodide with 50 c.c., but in the case of 0·2% chloride in bromide, if 50 c.c. are used the breaks in the curve are not separated, and at least 100 c.c. must be taken.

The estimation of low percentages of chloride in iodide or bromide thus involves taking a big bulk of material; this makes the titration very long, and introduces a possible source of error in that some of the chloride solution may be occluded in the bulky silver bromide or silver iodide precipitate. Means were therefore sought by which

the bromide or iodide could be destroyed, at the same time leaving the chloride free in the solution, where it could be titrated.

Numerous methods have been devised for estimating mixtures of halides in which one halogen is removed by oxidation of its halide salt, leaving the other halide intact. Considering a chloride–bromide mixture, however, it is very probable that in the region of the point where practically all the bromide had been destroyed, some of the chloride would be attacked as well. A satisfactory method of operation would be to react with insufficient oxidiser to destroy all the bromide present, leaving, say, equal proportions of bromide and chloride, and then to titrate this mixture electrometrically in the usual way. In this manner, a big bulk of mixture, in which the absolute amount of chloride is high enough for the accuracy required, can be used without the disadvantages already mentioned. There seems theoretically to be no limit to the minuteness of the trace of chloride which could be estimated in this way.

Attempts to destroy all the bromide by means of ammonium persulphate (Engel. Compare Crookes's "Select Methods in Chemical Analysis," 1905, p. 558) or potassium permanganate (Winkler, *Z. angew. Chem.*, 1915, **28**, 477, 494) were not successful. In the former case all the bromide could not be destroyed, even when many times the theoretical quantity of persulphate was used, whilst in the latter case some chlorine was always lost in getting rid of the last traces of bromide. For example, a mixture of 2·3800 g. of pure potassium bromide with 0·0050 g. of potassium chloride in 350 c.c. of water was analysed by Winkler's permanganate method, and 0·0038 g. of chloride was found instead of 0·0050 g.

Using just insufficient permanganate to react with all the bromide proved to be a very suitable and accurate means of determining low percentages of chloride in iodide and bromide. The procedure is best illustrated by an actual example, as follows: A mixture of 2·3800 g. of potassium bromide and 0·0050 g. of potassium chloride was dissolved in 350 c.c. of water, 25 c.c. of concentrated sulphuric acid were added, and the whole was boiled. A solution of *N*/2-chloride-free potassium permanganate was prepared. A blank test having shown that 43·5 c.c. of this solution were necessary to give a permanent pink colour with the halide mixture used, 43·0 c.c. of permanganate were added slowly to the boiling acidified halide solution, and boiling was continued until all the bromine was removed and the solution became colourless. Ammonium nitrate (10 g.) was dissolved in the solution, which was then cooled and titrated electrometrically with *N*/100-silver nitrate. The result was: chloride taken, 0·0050; found, 0·0051 g.

The presence of manganous salts in the titration beaker does not affect the titration adversely in any way. Owing to the presence of sulphuric acid in the solution, it is preferable to add ammonium nitrate or sodium acetate, rather than barium nitrate, for the titration. Although a titration carried out with barium sulphate present gave accurate results, its presence is best avoided if the possibility of occlusion is to be eliminated.

Estimation of Low Percentages of Bromide in Chloride.

Although percentages of chloride in bromide from 50% down to 0·2% have been shown capable of accurate estimation, very low percentages of bromide in chloride cannot be accurately determined by direct electrometric titration. It has been found quite impossible, by direct methods of electrometric titration, to determine bromide present to the extent of less than 5% in chloride.

The following observations were made with 5% bromide in chloride of $N/10$-strength: (*a*) with 20 c.c. of mixture + 150—200 c.c. of 5% ammonium nitrate titrated with $N/100$-silver nitrate, a curve was obtained, with no sign of a sharp break, but merely a slight increase of slope over a long range of c.c. silver nitrate added.

(*b*) (*a*) was repeated in presence of saturated ammonium nitrate solution with the same results.

The absence of a sharp break is peculiar. When a mixture of, say, equal proportions of chloride and bromide is titrated, the composition varies until it passes through a stage at which there is 5% bromide in chloride, and yet a sharp bromide end-point is obtained. The only difference between this and the cases (*a*) and (*b*) above is that there is a bulk of silver bromide present, owing to precipitation of the first 45% of bromide.

(*c*) In order to simulate these conditions, 20 c.c. of $N/10$-ammonium bromide were titrated to the end-point with $N/10$-silver nitrate. 20 C.c. of $N/10$-5% bromide in chloride were then added, and the titration was continued with $N/100$-silver nitrate. The same results were found as in (*a*) and (*b*). By plotting the curves of (*a*), (*b*), and (*c*) on a more closed scale, a fairly sharp increase of slope was observed in the neighbourhood of the theoretical end-point, but it was impossible to locate the end-point with any degree of certainty.

Titration with $N/100$-silver nitrate is thus useless for determining 5% of bromide in chloride. The only way of obtaining satisfaction seemed to be to work with a higher concentration of silver nitrate, and a bigger bulk of halides.

(*d*) 10 C.c. of 5% bromide in chloride + 50 c.c. of 5% barium nitrate, titrated with $N/10$-silver nitrate, gave a sharp break at

0·5 c.c. of silver nitrate, the theoretical value. The degree of accuracy to be expected with a titre of 0·5 c.c. is, however, low.

(*e*) (*d*) was therefore repeated with 100 c.c. of 5% bromide in chloride. Solid ammonium nitrate was dissolved in this, and it was titrated with *N*/10-silver nitrate. A definite break was obtained in the titration curve, and its inflexion point being taken as the bromide end-point, the theoretical bromide value was found. A quotation from Müller has already been cited, in which he states that bromide cannot be accurately determined in presence of chloride, unless the molar concentration of bromide exceeds that of chloride by five times.

As shown above, however, it is possible to estimate 5% bromide in chloride of *N*/10-strength by titration of 100 c.c. with *N*/10-silver nitrate. Percentages less than 5 cannot be so estimated with any degree of accuracy. The difficulty could probably be overcome by adding a known amount of bromide to adjust the ratio of Br^- : Cl^- to 1 : 1, titrating this mixture, and obtaining the original bromide by difference. The objection to this seems to be that any error in the titration of the total halide would be thrown on to the small percentage of bromide originally present.

Müller ("Elektrometrische Massanalyse," 2nd edn, 1923, p. 95), titrating 5% bromide in chloride directly, got accurate results * in presence of barium nitrate, but a + 16% error in the bromide in absence of barium nitrate. With a 2·5% bromide in chloride he got an error of + 16% in presence of barium nitrate, and + 36% in absence of added salts. These results have been substantially confirmed in the experiments described here.

To estimate low proportions of bromide in chloride it thus appeared necessary to isolate the bromide as bromine either free from chlorine, or else with such an amount of chlorine as to give a preponderance of bromine, convert the bromine (and chlorine) into bromide (and chloride), and then titrate the bromide electrometrically. The presence of a small amount of chloride from chlorine carried over with the bromine will not be harmful, since, as has been shown, low ratios of chloride in bromide can be readily estimated.

Removal of bromine with bromate in acid solution was first tried. The method was satisfactory for 28·6% bromide in chloride, but for 1% bromide, it gave very variable results, and was therefore abandoned.

The use of permanganate proved to be satisfactory. The apparatus consists of a conical flask fitted with a stopper (preferably

* This appears from Müller's table (p. 95) to be just a chance accuracy, and is contradictory to a statement by Müller quoted earlier in this paper.

of glass, ground in) carrying a graduated tap funnel for the permanganate, and a tube with a trap, leading to a vertical condenser dipping into ammonia in a receiving flask. The bromide–chloride mixture is put in the conical flask together with plenty of sulphuric acid and boiled. Permanganate is run in drop by drop until the pink colour persists for a short time, and then a further addition of about the same volume of permanganate is made, and the solution is boiled for some time, until it loses its colour. The ammonia in the receiver is acidified, ammonium nitrate added and the solution titrated as usual. The following figures show that this method is capable of a fair degree of accuracy :

	Bromide in chloride.	
Mixture examined.	Theoretical %.	% Found.
200 C.c. of 1% bromide in chloride (N/10).	1	(1) 0·95 (2) 0·9
40 C.c. of 0·5% bromide in chloride (N/10).	0·5	0·49

A further attempt to estimate bromide in chloride was made using the method of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 623), in which the halides are mixed with potassium cyanide solution and sulphuric acid and titrated electrometrically to the CNBr end-point with permanganate solution. The method was tried with a platinum electrode and calomel cell, but the potential readings were very inconsistent and jerky, and the rate of attainment of equilibrium of potential was very variable. The method of Willard and Fenwick depends on the same reaction as that employed by Müller and Schuch (*Z. Elektrochem.*, 1925, **31**, 332) for estimating halogens in solution by electrometric titration with cyanide. Various modifications of this method were tried without success.

The ingenious method of " differential titration " due to Cox, already mentioned, was investigated for the titration of bromide with silver nitrate, and good results were obtained. An example of the method used is as follows : 10 c.c. of N/10-bromide + 200 c.c. of water were put into each of two beakers. The solutions were united by a bridge of saturated ammonium nitrate solution, and silver electrodes were immersed one in each solution and connected to the potentiometer. The two solutions were titrated simultaneously with N/10-silver nitrate from two burettes, one being kept 0·2 c.c. ahead of the other, the *E.M.F.* being measured after each addition of silver nitrate as usual. A very sharp maximum was obtained, and equilibrium was practically instantaneous. Bromide found = 20·1 c.c.; theoretical = 20·14 c.c. of N/10-$Ag^{\cdot}$. The method is thus satisfactory for plain bromide solution. Its advantages are that it eliminates the use of the calomel cell, and

equilibrium is instantaneous at the end-point. Its disadvantage is that manipulation of two burettes is necessary. On the whole, however, it appears to possess no ultimate advantage over the ordinary method.

The differential method was tried for the estimation of 1% bromide in chloride, but without success. At the bromide end-point the curve certainly tended to a maximum, but this could not be definitely located.

Estimation of a Mixture of Three Halides.

Since a pair of soluble halides can be estimated accurately under certain conditions, it is to be expected that a mixture of three halides could just as accurately be determined under similar conditions.

A mixture containing 3% iodide and 1% chloride in $N/10$-bromide was examined. This ratio represents possible proportions of halide in a photographic preparation. 20 C.c. of the mixture + 200 c.c. of 5% barium nitrate solution were taken; the bulk was titrated with $N/10$-silver nitrate and the end-points were determined with $N/100$-silver nitrate. Taken: bromide, 19·48; chloride, 0·23; iodide, 0·59. Found: bromide, 19·48; chloride, 0·22; iodide, 0·59 (the figures denote equivalents of $N/10$-silver nitrate).

Analysis of Silver Halides.

In the analysis of silver halides by electrometric methods, two methods of procedure are possible. The first is to dissolve the silver halides in a suitable solvent and titrate directly the solution obtained. The second method is to set free the halogen from the silver halides in the form of soluble halides, which can be readily titrated by the normal methods.

The only method of the first type known to the author is that due to Müller (*Phot. Ind.*, 1924, 305, 332). The silver halides are dissolved in a slight excess of potassium cyanide solution, and the resulting solution is titrated electrometrically with silver nitrate. The theory of the titration and the method of deducing the results are lucidly described in Müller's original paper. Müller claims satisfactory results in the titration of a single silver halide, and with mixtures of silver iodide with silver bromide or silver chloride. Numerous measurements made to check the accuracy of the method have fully substantiated Müller's claims. The method suffers, however, from a serious limitation in that it does not distinguish between silver bromide and silver chloride. In the analysis of many photographic materials this should be of no account, since the majority of fast plates should consist entirely of silver bromide

and silver iodide mixtures. In the case of some plates, however, chloride is added in addition to the other two halides, and in most cases chloride is present unintentionally because the soluble iodide and bromide used in making the emulsions are rarely, if ever, free from chloride. For the analysis of chloro-bromide emulsions, Müller's method would obviously be unsuitable.

Owing to the limitations of Müller's method, the second type of method, in which the silver halides are converted into soluble halides, was investigated. Samples of pure silver halides were first prepared in the following manner. The preparations were carried out in red light, and the products were stored in dark brown glass bottles.

Silver chloride was prepared by adding silver nitrate drop by drop to a vigorously stirred solution of pure potassium chloride until the slightest excess of chloride remained. The precipitate was washed many times with water, and drained by suction. One sample of chloride was dried in a desiccator, but formed such hard lumps that it could not readily be dissolved in cyanide solution. The moist preparation was therefore used.

Silver bromide was prepared from a sample of commercial potassium bromide containing about 1% of chloride. It was dissolved in 5% ammonium nitrate solution, and silver nitrate, also in 5% ammonium nitrate solution, was run in drop by drop, the whole being vigorously stirred. Silver nitrate equivalent to 14/17 of the bromide was added during 3 hours. The precipitate was washed five times by decantation, collected, and dried in a desiccator.

Silver iodide. Part of the damp sample made for the preparation of pure soluble iodide, as described earlier, was dried in an electric oven at 105°.

Conversion of the Silver Halides into Soluble Halides.

Two methods of reduction of the silver halides to give the halogen in the form of soluble halides were investigated: (*a*) Direct reduction of the solid silver halide. (*b*) Reduction of the silver halide in solution.

Method (*a*).—The simplest method of getting the halide in the soluble form is direct reduction of the solid silver salt by a substance such as hydroxylamine. For electrometric titration it is necessary that the excess of the reducing agent be rendered harmless in some simple way which does not involve any loss of halogen.

Destruction of any excess of hydroxylamine could be satisfactorily carried out by gentle ignition with excess of alkali at about 200°. Oxidising agents, which would probably cause loss of halogen, should not be used.

Formic acid was unsuitable as a reducing agent, even on prolonged boiling with the silver salts. Reduction was far from complete, and chocolate-brown products resembling the synthetic photo-halides were formed. Hydroxylamine sulphate in alkaline solution was very efficient, but the reduction of solid silver halides by its means, even on very prolonged stirring, was incomplete in the majority of cases. The spongy silver mass obtained invariably contained traces of unreduced silver halide, which could be detected by dissolving the silver in nitric acid. Attempts were made to peptise the silver halides before reduction and thus render the reduction quantitative. Octyl alcohol was useless for this purpose. Addition of a known excess of potassium iodide gave a finely-divided suspension in the case of silver iodide, but the excess of halogen ions slowed down the rate of reduction so much as to render its use impracticable.

Boiling a suspension of silver iodide in water with zinc and dilute acetic acid gave incomplete reduction.

Method (*b*).—Reduction of the solid halide having proved useless for obtaining quantitative conversion to soluble halide, the reduction of the solution of the silver halides in potassium cyanide solution was investigated. A solution of silver iodide in cyanide was treated with (*a*) alkaline hydroxylamine, (*b*) alkaline hydrazine hydrate, (*c*) sodium hydrosulphite [hyposulphite], and (*d*) diaminophenol (amidol). With (*a*) there was no reduction in 18 hours, and with (*b*) in the same time, only a trace of action. Hydrosulphite reduced the solution directly to silver; and amidol caused reduction on long standing, but there was simultaneous formation of undesirable oxidation products.

When hydrosulphite is added to a solution of silver iodide in cyanide, precipitation of the silver iodide first occurs, and this is followed rapidly by its reduction. If the solutions are too concentrated, coagulation of the silver iodide occurs before it is reduced, and results in a part of the silver halide inside the curds remaining unreduced. Complete reduction of the silver halide can be effected by working in dilute solution, and adding the hydrosulphite solution a little at a time. On each addition a yellow colloidal solution of silver iodide forms. The next addition of hydrosulphite should not be made until reduction of the colloidal suspension due to the previous addition begins.

Attempts were made to prevent coagulation of the silver iodide by adding colloids before reduction. Gelatin and gum arabic effectively prevented coagulation, but their use resulted in the formation of a protected colloidal silver sol on reduction, and this could not be removed by filtration, even after prolonged boiling

with electrolytes. More satisfactory results were obtained with dextrin; the silver formed on reduction with hydrosulphite readily coagulated on boiling, and could be filtered off.

The excess hydrosulphite can be destroyed by boiling with acid, which also removes all the cyanide ions, and the solution of soluble halides is then ready for titration, after addition of barium nitrate or other salt.

Almost all commercial samples of sodium hydrosulphite contain appreciable quantities of chloride. This makes the hydrosulphite method dependent on the ability to obtain the chloride-free product, the application of a correction for chloride being undesirable. Attempts made to prepare pure hydrosulphite as required, *e.g.*, by passing sulphur dioxide gas into water containing metallic zinc, or into a solution of sodium sulphite containing zinc were not satisfactory. Combination of the two operations of preparing hydrosulphite and reducing the silver complex by passing sulphur dioxide into a cyanide solution of silver iodide containing sodium sulphite and metallic zinc did not give very satisfactory results.

Reduction with Zinc.—Although hydrosulphite is very satisfactory for reducing the cyanide solution, the difficulty of getting samples free from chloride led to trials with other reducing agents, of which zinc dust or granulated zinc, with acetic acid, proved very satisfactory.

Boiling the solution with granulated zinc and acetic acid gives complete reduction. On adding the acetic acid there is a tendency to form colloidal silver halide, but although in certain cases coagulation sets in, it is not of such a nature as to prevent complete reduction to silver. Addition of sodium acetate to the acetic acid, lowering the acidity to p_{H} 4·8, did not prevent some silver salt being thrown out of solution.

Results as satisfactory as those obtained with granulated zinc and acetic acid are obtained by boiling with granulated zinc or zinc dust without acid, and no precipitation of silver halide occurs in these cases. It is necessary, however, to add acetic acid after the reduction is over in order to remove the excess of cyanide. The disadvantage in the case of zinc dust is that many samples contain chloride, whereas granulated zinc can be readily obtained very pure.

The conditions for titration of the reduced solution are as follows :

(1) No free cyanide must be present. This is ensured by boiling with acetic acid.

(2) Presence of free acetic acid has no adverse effect on the titration of mixed halides. In fact, sodium acetate has been shown to be advantageous.

(3) Undissolved zinc must be filtered off, otherwise further reduction will occur during the titration with silver nitrate.

(4) Zinc ions present in the titration must have no adverse effect. That they do not affect the titration was shown by control titrations to which zinc sulphate had been added.

(5) Boiling a solution of soluble halide with zinc and acetic acid must not result in loss of halogen. Blank experiments showed that no such loss occurred.

The method was then tested quantitatively, with known amounts of standard solutions of silver halides in potassium cyanide. Müller's titration method (*vide supra*) was employed for standardising these solutions. Use of this method for estimating known weights of silver halide in cyanide solution gave very accurate results, and justified its use for the standardisation of solutions. 20 C.c. of the standard solutions of silver iodide, bromide, and chloride were equivalent to 17·20, 27·10, and 7·65 c.c., respectively, of $N/10$-silver nitrate.

Both granulated zinc and zinc dust reduction gave accurate results with all three halides. The method finally used in all cases is illustrated by the following example:

Stock silver iodide–potassium cyanide solution (20 c.c.) was diluted to about 100 c.c. with water and heated, 1—2 g. of granulated zinc in small pieces were added, the solution was boiled vigorously for 10—15 minutes, 50 c.c. of acetic acid (100 c.c. of glacial acid diluted to 1 litre with water) were added, and boiling was continued vigorously until all smell of cyanide had disappeared. The solution was then cooled and decanted through a filter, the metallic residue being carefully washed several times. Ammonium nitrate was added to the combined filtrate and washings to make about 5% concentration, and titration was carried out electrometrically in the manner already described.

The quantities taken and found, expressed as c.c. of $N/10$-silver nitrate, were: silver iodide, 17·20 and 17·20; silver bromide, 27·10 and 27·10, 27·05; silver chloride, 7·65 and 7·65. The conversion of silver halide into soluble halide is thus quantitative. There should therefore be no more difficulty attending the estimation of mixed silver halides than was the case with mixtures of soluble halides already described. For this reason, exhaustive investigation of mixed silver halides was not made. For two mixtures of silver iodide and silver bromide, reduced with zinc and acetic acid, the values, in c.c. of $N/10$-silver nitrate, were: (1) Bromide: taken, 27·10; found, 27·05. Iodide: taken, 4·30; found, 4·30; (2) Bromide: taken, 27·10 found, 27·09. Iodide: taken, 0·43; found, 0·41.

Analysis of Photographic Emulsions.

The method described above was applied to the analysis of photographic emulsions.

Preliminary experiments were made to ascertain whether the reduction of silver halides could be satisfactorily carried out in presence of gelatin. A mixture of standard potassium cyanide–silver iodide solution, 100 c.c. of water, and 25 c.c. of 1% gelatin was heated to boiling, granulated zinc and 50 c.c. of 10% acetic acid were added, and the boiling was continued. In ½ hour very little reduction had occurred, and the silver halide which had been thrown out of solution was carried away from the sphere of reduction by the frothing gelatin. Several hours' boiling had not resulted in complete reduction.

In another case, the emulsion was scraped off a soaked photographic plate into water, which was heated to disperse the gelatin. Cyanide was added to dissolve the silver salts, and the whole was boiled with zinc and acetic acid. After several hours, reduction was again incomplete.

It was obvious that the presence of gelatin was to be avoided. If the emulsion is boiled with nitric acid to destroy the gelatin there is an element of risk involved, in view of the known action of nitric acid in freeing halogen from silver halides. Lehmann and Bolmer (*Phot. Ind.*, 1922, 467, 491) found that cold nitric acid above a concentration of 47%, and hot nitric acid above 5%, converts silver iodide into silver nitrate and iodine. If, however, 5% nitric acid is used for destroying the gelatin, the halide remains in suspension and cannot be filtered. The workers mentioned recommended a mixture of 4% nitric acid in 20% acetic acid for isolating the silver halide. Valenta (*Phot. Korr.*, 1914, **51**, 122; "Photographische Chemie und Chemikalienkunde," I, 2nd edn, 1921, p. 151) used 20% nitric acid for destroying the gelatin. This practice is criticised by Lehmann and Bolmer, and is shown to lead to errors.

It appeared preferable to avoid the use of oxidising acids for the destruction of the gelatin, in the case of plates, at any rate. The method of fixing out the silver halides with cyanide was therefore tried, with success; this has the advantage of eliminating the need for stripping the emulsion.*

Numerous commercial plates were investigated, to ascertain the best conditions for analysis. With plates of fast, or special rapid

* If stripping is considered desirable, it can readily be carried out by means of alkaline sodium benzoate, prepared by dissolving benzoic acid in excess of caustic soda solution.

type, one half-plate provides a suitable quantity of material for investigation, but in the case of thinly-coated plates of the process type, two half-plates should be used.

The method of analysis finally adopted for a half-plate is as follows :

The plate is fixed out in a dish with 100 c.c. of $N/10$-potassium cyanide, and washed by soaking (5 minutes) in three changes of 100 c.c. of water. No silver salts can, in general, now be detected in the gelatin film. As a precaution, however, after washing, the plate is spotted with sodium sulphide; the absence of a brown stain indicates freedom from silver salts. The washings and fixing solution are combined, reduced with zinc and acetic acid, and treated as described for the examination of mixed silver salts. $N/100$- or $N/10$-Silver nitrate is used for titration, according to the amount of the particular halide being analysed. Owing to a slight action of the cyanide solution on the gelatin of the plate, a little gelatin sometimes goes into solution, but it only results in a somewhat slower attainment of equilibrium of potential when dilute silver nitrate is used. With $N/10$-silver nitrate, equilibrium is attained at the normal rate.

The following table shows the results obtained in the analysis of a few commercial plates. These plates were of *unknown* composition, and so no check on the results was available.

Plate.	Size.	AgI.	AgBr.	Total halide.	% AgI.
A. Special rapid.	¼	0·41	6·74	7·15	5·73
B. „ „	¼	0·47	8·18	8·65	5·44
C. „ „	½	0·52	13·88	14·40	3·61
D. „ „	½	0·55	13·61	14·16	3·88
E. Process.	½	0·11	9·30	9·41	1·17

Plates A and B were of one brand. It does not follow from this that they are of identical composition, since variations often occur among plates of the same manufacture. Also it is improbable that the total amount of silver halide is identical on both plates. Similar remarks apply to C and D. The values in columns 3, 4, and 5 refer to c.c. of $N/10$-silver nitrate equivalent to the halides.

At the time when these measurements were made, only one emulsion of accurately known composition was available. Duplicate analyses were made of half-plates hand-coated with this emulsion, with the following results :

	AgI.	AgBr.	Total halide.	% AgI. Found.	% AgI. Theor.
Plate 1	0·81	19·83	20·64	3·92	3·95
Plate 2	0·80	19·57	20·37	3·92	3·95

The method thus appears capable of giving accurate results. It possesses the great advantage of ease and comparative rapidity.

The author wishes to express his gratitude to Dr. T. Slater Price, F.R.S., Director of Research to the British Photographic Research Association, for the interest he has taken in this work, and for the valuable criticism and advice he has given.

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CV.—*The Absorption Spectra of Various Derivatives of Salicylic Acid.*

By JOHN EDWARD PURVIS.

THE author described (J., 1925, **127**, 2771) the absorption spectra of various compounds derived from salicylic acid in order to compare the influence of different types of nuclei. The investigation has been continued with the following coloured and colourless salts and other compounds of the acid. The substances were examined in the first instance in *M*/200-solutions, with the exceptions of 3-nitrosalicylic acid and 5-aminosulphosalicylic acid, which were not so soluble. These were examined in *M*/2000- and *M*/20,000-solutions.

Lithium, calcium, and zinc salicylates. The curves (Fig. 1, upper curves) show in the lithium compound a band at $1/\lambda$ 3350 (λ 2984) comparable with that of salicylic acid (*loc. cit.*), but the more refrangible band between $1/\lambda$ 4120 (λ 2425) and $1/\lambda$ 4300 (λ 2320) is not so well marked as that in salicylic acid. In the calcium and zinc salts, somewhat similar phenomena were noticed; and there are differences in the positions of the bands dependent on the respective molecular weight. The less refrangible band of the monobasic lithium salt is not, of course, so strong as that of the calcium and zinc salts.

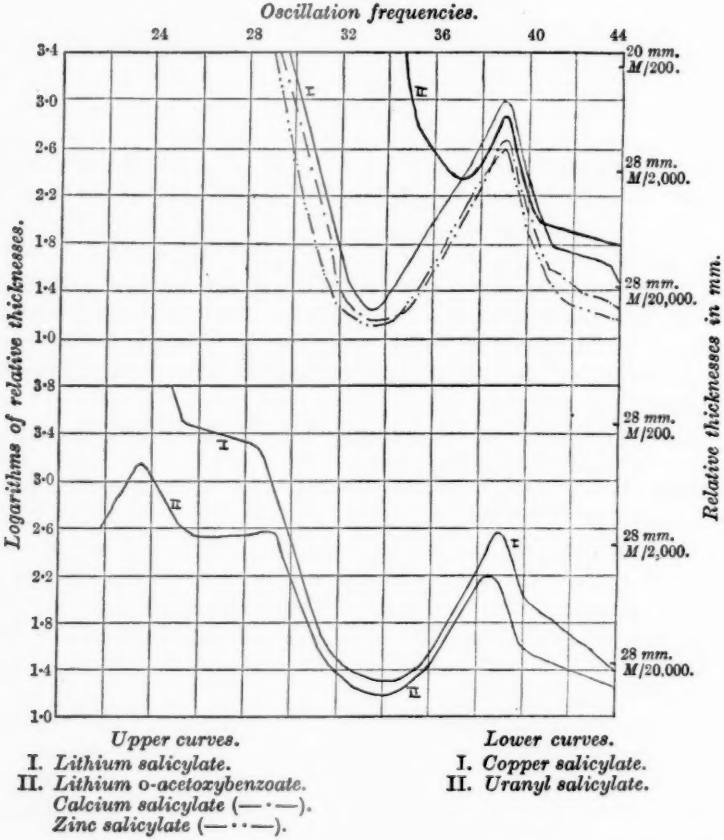
Lithium o-*acetoxybenzoate* (Fig. 1, upper curves). The replacement of the hydroxyl hydrogen atom by the acetyl group has produced a similar change to that in salicylic acid and *o*-acetoxybenzoic acid, and in theobromine salicylate and theobromine *o*-acetoxybenzoate (*loc. cit.*). The less refrangible band at $1/\lambda$ 3740 (λ 2672) is very weak and is shifted towards the more refrangible regions; and the more refrangible band is represented by a more rapid extension of the rays from about $1/\lambda$ 4020 (λ 2486). As the author has previously pointed out in the case of *o*-acetoxybenzoic acid, this has produced an absorption comparable with that of benzoic acid.

Copper salicylate (bluish-green). The curve (Fig. 1, lower curves)

shows the less refrangible band of salicylic acid well developed, and the more refrangible one is nearly obliterated. There is a rapid absorption of the rays between about $1/\lambda$ 2850 (λ 3506) and $1/\lambda$ 2550 (λ 3919), extending well into the visible region.

Uranyl salicylate (reddish-brown). The curve (Fig. 1, lower curves) has a somewhat similar form to that of copper salicylate,

FIG. 1.



Upper curves.
I. *Lithium salicylate.*
II. *Lithium* o-*acetoxybenzoate.*
Calcium salicylate (—·—).
Zinc salicylate (—··—).

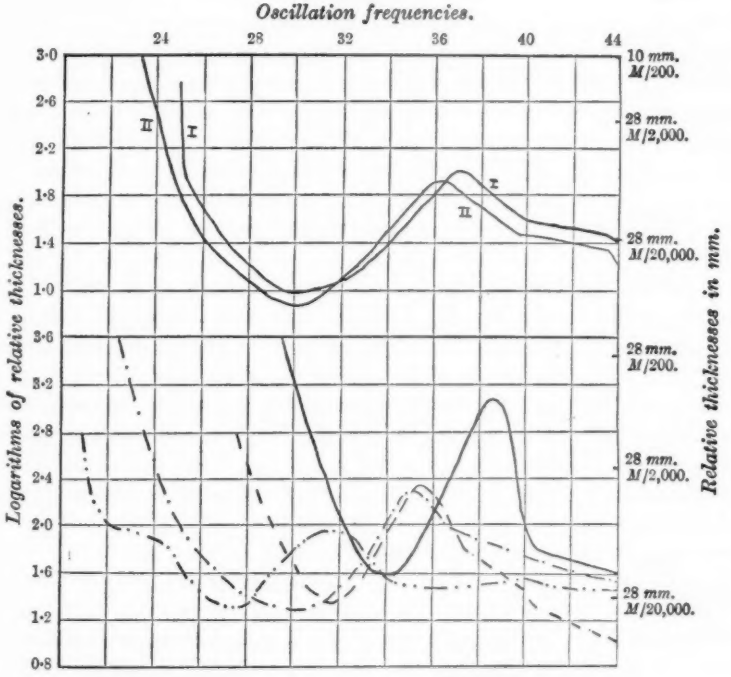
Lower curves.
I. *Copper salicylate.*
II. *Uranyl salicylate.*

but the band between $1/\lambda$ 2940 (λ 3400) and $1/\lambda$ 2520 (λ 3967) is better marked, and there is another band on the less refrangible visible parts at about $1/\lambda$ 2200 (λ 4544). The band at $1/\lambda$ 3400 (λ 2940) is wider than the corresponding band of the copper salt.

3-*Nitrosalicylic acid* (yellow), 3 : 5-*dinitrosalicylic acid* (yellow). In each of these substances there is a large band extending into the visible region (Fig. 2, upper curves), and it is much wider than

the corresponding bands of the substances described above. The more refrangible band is merely indicated by the more rapid extension of the rays from $1/\lambda$ 4000 (λ 2498) to $1/\lambda$ 4400 (λ 2271) in the nitro-compound, and from $1/\lambda$ 3920 (λ 2550) to $1/\lambda$ 4350 (λ 2298) in the dinitro-compound. These results are not unlike those described by the author (J., 1915, **107**, 966) in the case of some nitro-compounds of benzoic and cinnamic acids.

FIG. 2.



Upper curves.

I. 3-*Nitrosalicylic acid.*
II. 3 : 5-*Dinitrosalicylic acid.*

Lower curves.

5-*Sulphosalicylic acid* (——).
5-*Aminosulphosalicylic acid* (— —).
5-*Nitrosulphosalicylic acid* (— · — · —).
Sodium salt of 3-nitro-5-aminosalicylic acid (— · · —).

5-*Sulphosalicylic acid*, 5-*aminosulphosalicylic acid.* These two substances show (Fig. 2, lower curves) that the more refrangible band of salicylic acid is not so definite, but in each case the less refrangible one is well marked. In the amino-compound this band is not quite so strong as it is in the sulpho-compound, and there are differences in the persistency.

5-*Nitrosulphosalicylic acid* (yellow). There is a wide band

(Fig. 2, lower curves) at $1/\lambda$ 3000 (λ 3344) not unlike that of the other nitro-compounds, and extending into the visible region. The more refrangible one almost disappears.

Sodium 3-nitro-5-aminosalicylate (reddish-brown). This substance (Fig. 2, lower curves) exhibits a large band at $1/\lambda$ 2750 (λ 3633) which extends rapidly into the visible regions. This band may be compared with that of the other nitro-compounds. There is also a shallow band from about $1/\lambda$ 3400 (λ 2939) to $1/\lambda$ 3930 (λ 2543).

Hexamethylenetetramine, Hexamethylenetetramine salicylate. Through 56 mm. thickness of a *M*/200-solution hexamethylenetetramine exhibited no band; and the rays were transmitted to λ 2150. Its salicylate, on the other hand, exhibited an absorption band comparable with that of salicylic acid. Paraldehyde shows no specific absorption (J., 1925, **127**, 9); and it is suggested that, like paraldehyde, the condensation of formaldehyde with ammonia in the production of hexamethylenetetramine neutralises the free valencies of the aldehydic oxygen which produce a band in formaldehyde itself.

Results.—Considering these results with those of salicylic acid and its various salts (*loc. cit.*), it appears that the specific absorption of the substances depends on the nature of the basic and of the acid radicals. Changes in the nature of the one or the other produce changes in the position and intensity of the bands characteristic of each. The author has already shown, in a study of the absorption spectra of some organic and inorganic salts of didymium (*Proc. Camb. Phil. Soc.*, 1923, **21**, 781), that the bands of didymium in the visible regions were modified in intensity according to the type of the negative radical united with this base.

As regards the other derivatives of salicylic acid, the influence of the nitro-group in the benzene radical powerfully intensifies and shifts the less refrangible band of the acid, but appears to lessen that of the more refrangible one. Also the replacement of the hydrogen atom of the hydroxyl group by a radical, as in lithium salicylate and lithium *o*-acetoxybenzoate, changes the absorption capacity of the other parts of the molecule; and this is comparable with the phenomena of *o*-acetoxybenzoic acid, and of the *o*-acetoxybenzoates of theobromine and quinine.

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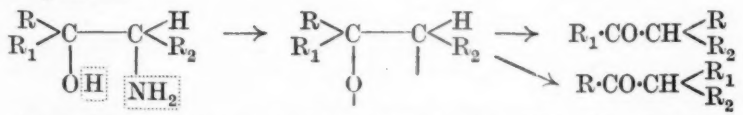
CVI.—*Elimination of the Amino-group of Tertiary Amino-alcohols. Part III. A New Method for the Preparation of Optically Active Ketones.*

By ALEX. MCKENZIE, ROBERT ROGER, and GEORGE OGILVIE WILLS.

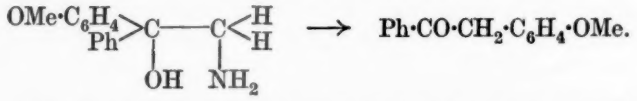
PREVIOUS research (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, J., 1924, **125**, 2105; McKenzie and Wills, J., 1925, **127**, 283) carried out in this laboratory on the behaviour of certain tertiary amino-alcohols towards nitrous acid has demonstrated that in no case was the glycol corresponding with the amino-alcohol isolated, although such glycols are readily enough accessible in other ways. The action is thus an abnormal one, the product invariably being a ketone (a dehydration product of the glycol). At once the simplest and the most obvious interpretation would be based on the assumption that the glycol is formed as an intermediate phase and then undergoes dehydration. This is an assumption which is, however, untenable, and the experimental evidence is conclusive in proving that a hydrocarbon residue migrates from one carbon atom to another adjacent to it. A process, such as this, for effecting the migration of groups was designated by McKenzie and Roger as "semipinacolinic deamination" from its analogy with the semipinacolinic changes which have come under the observation of Tiffeneau, Orékhov, and their colleagues.

The latter chemists, as well as Meerwein, have studied the dehydration of glycols where the two hydroxyl groups are bound to contiguous carbon atoms by gripping forces which vary in intensity. Wherever the variation of this gripping force is very great, that is to say, when the one hydroxyl group is very firmly and the other very loosely bound, the investigation of the dehydration of a glycol does occasionally provide a good indication of the migrational aptitude of groups. But, especially in other cases, semipinacolinic deamination is proving of service where the evidence deduced from the dehydration of glycols as to migrational aptitude is rather inconclusive. In fact, the method possesses the advantage of being a general one for testing the migrational aptitude of groups, as the elimination of the amino-group necessarily involves group transposition:

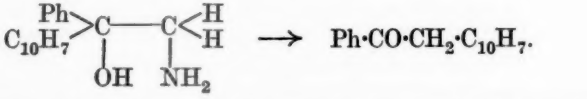


An extension of the method has lately been published by Orékhov

and Roger (*Compt. rend.*, 1925, **180**, 70) to embrace tertiary amino-alcohols where the amino-group is attached to a secondary carbon atom. Thus, the action of nitrous acid on β-hydroxy-ββ-diphenylethylamine leads to the formation of deoxybenzoin and not of *as*-diphenylethylene oxide, whilst the interpretation advanced by us agrees with that of Orékhov and Roger. Again, the superiority of the migrational aptitude of the *p*-anisyl as compared with the phenyl group is shown by the formation of *p*-methoxydeoxybenzoin from β-hydroxy-β-phenyl-β-anisylethylamine:

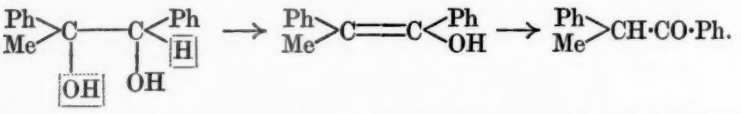


Further, when β-phenyl-β-(α-)naphthylethylamine is deaminated (Luce, *Compt. rend.*, 1925, **180**, 145), the naphthyl group wanders more readily than does the phenyl group, since ω-α-naphthylacetophenone is formed:



In the present paper, an application of our method to optically active amino-alcohols is described. The products are ketones, and it is remarkable that *optical activity is preserved in spite of the molecular rearrangement which is involved.*

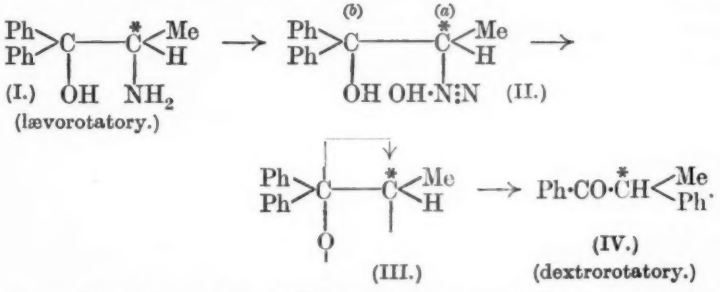
It may be recalled that in the formation of diphenylacetone from β-hydroxy-αβ-diphenylpropylamine a phenyl group migrates from a carbon atom to the adjacent one to which a phenyl group is already attached, and it would not therefore be anticipated (since diphenylacetone does not possess an asymmetric carbon atom) that the resulting ketone would be optically active if the starting point were the optically active amino-alcohol. The action of concentrated sulphuric acid on methylhydrobenzoin, the glycol corresponding with the above amino-alcohol, forms a striking contrast to the above, inasmuch as there is no group wandering, the change being what Tiffeneau calls "vinyl dehydration":



Now when the dextrorotatory methylhydrobenzoin, obtained by acting on *l*-benzoin with magnesium methyl iodide, is dehydrated with concentrated sulphuric acid, the resulting methyldeoxybenzoin is optically inactive, as it would necessarily be if the mechanism of

the action were that of vinyl dehydration. But McKenzie and Roger (J., 1924, **125**, 2148) have shown that, when the dehydrating agent is dilute sulphuric acid, the optical activity does not disappear; the product is not, however, an optically active methyldeoxybenzoin, but the lævorotatory diethylenic oxide, $\left(\begin{matrix}\text{CPhMe·CHPh}\\ \text{O}\end{matrix}\right)_2$. It is possible that the *r*-methyldeoxybenzoin, which is formed when concentrated sulphuric acid is employed, is produced from the lævorotatory diethylenic oxide formed as an intermediate phase, whilst racemisation accompanies the transformation of the oxide into the *r*-ketone.

In the experimental section, the preparation of *d*-methyldeoxybenzoin is described. *d*-Alanine was converted into its ethyl ester hydrochloride, from which l-β-*amino*-αα-*diphenyl*-n-*propyl alcohol* was obtained by the action of magnesium phenyl bromide.* When the amino-alcohol, with $[\alpha]_D - 82°$ in chloroform, is acted on by nitrous acid, it gives the *d*-ketone with $[\alpha]_D + 207°$ in the same solvent. On the interpretation of semipinacolinic deamination, the following mechanism is suggested:



In a discussion of the Walden inversion, Biilmann (*Annalen*, 1912, **388**, 330) depicts the action of silver nitrate on α-bromopropionic acid as taking place between the silver ion and the acid ion on the lines:

$$CH_3\cdot CHBr\cdot CO\cdot\bar{O} \text{ and } Ag^+ \longrightarrow CH_3\cdot\overset{+}{C}H\cdot CO\cdot\bar{O} \text{ and } AgBr.$$

The resulting "Zwitterion" then combines with the hydroxyl ion from water:

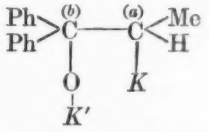
$$CH_3\cdot\overset{+}{C}H\cdot CO\cdot\bar{O} \text{ and } (OH)^- \longrightarrow CH_3\cdot CH(OH)\cdot CO\cdot\bar{O}.$$

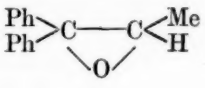
* The designations *d*- and *l*- throughout this paper mean dextrorotatory and lævorotatory, respectively, and do not refer to configurative relationships. The dextrorotatory alanine is converted in the above case into a lævorotatory amino-alcohol which is, however, configuratively related to the parent amino-acid.

Biilmann advanced this idea as a basis of some generalisations which are untenable, as they were framed on an imperfect recognition of the literature and were not in accordance with the experimental facts. McKenzie and Clough (J., 1913, **103**, 687), in their criticism of Biilmann's paper, pointed out that since a "Zwitterion" is supposed to be electrically neutral, it cannot even be urged that a free electric charge plays the part of the fourth grouping which is necessary for the retention of asymmetry. At the same time, the conclusion was drawn that if Biilmann's idea were accepted, the formation of an optically active structure containing a tervalent carbon atom must be admitted, a view for which there was not the slightest experimental evidence.

It might be submitted that such evidence is now forthcoming in the retention of asymmetry during the formation of *d*-methyldeoxybenzoin (IV) from *l*-β-amino-αα-diphenyl-*n*-propyl alcohol (I). Various interpretations could be advanced, and of these the one which we favour as being the least unsatisfactory is the following. After the elimination of the nitrogen from (II), the carbon atom (*a*), from which the nitrogen has been detached, retains an electric charge K; the oxygen atom attached to the contiguous carbon atom (*b*) also retains an electric charge K', so that (III) would be written thus (A):

(A.)





(B.)

Were those charges of opposite kinds, positive and negative, the formation of diphenylpropylene oxide (B) would have been anticipated instead of that of the isomeric methyldeoxybenzoin. Now diphenylpropylene oxide (Stoermer, *Ber.*, 1906, **39**, 2288) is a stable compound, which under the experimental conditions adopted would have been isolated if it had been formed. Since it is not formed, the assumption—a very problematical one—is made that the electric charges as pictured above are of the same sign, and repel one another. During the transposition of a phenyl group to carbon atom (*a*), we are dealing with a reaction of substitution, the charge K playing the part of a group and being displaced by a phenyl group which may or may not occupy the position vacated by the amino-group, so that on this picture *a Walden inversion is possible within the molecule itself.*

There is no evidence available as to whether *d*-methyldeoxybenzoin has the same configuration as the *d*-alanine from which it is prepared; so far as is known, it may equally well have the

opposite configuration. Now one of us in the course of work on the Walden inversion has shown that displacement racemisation very frequently accompanies the displacement of groups in optically active compounds, especially in such as have a phenyl group attached to the asymmetric carbon atom, and it is thus rather significant that the crude product from the deamination of the *l*-amino-alcohol gave a value for its specific rotation which is considerably below that of the optically pure ketone (see experimental part). In this product we probably had to deal with a mixture of the *r*- and *d*-ketones, from which the latter was easily isolated by repeated crystallisation.

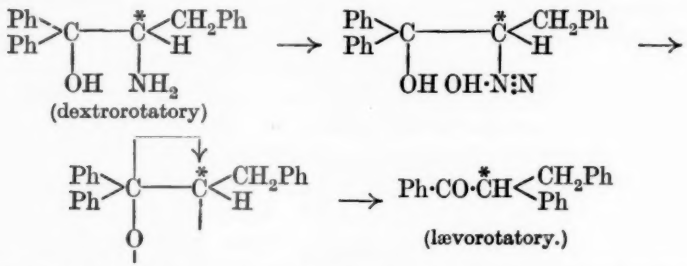
There are several examples on record where an electric charge is put forward as playing the part of a group in retaining asymmetry. For example, Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259) point out that the electronic formula for an aliphatic diazo-compound suggests the possibility of such a compound exhibiting optical activity, although this is not apparent from the formulæ either of Curtius or of Angeli and Thiele. Chiles and Noyes (*J. Amer. Chem. Soc.*, 1922, **44**, 1798) claim to have obtained several optically active aliphatic diazo-compounds which do not contain an asymmetric atom in the old sense of the term, thus diethyl diazoglutarate is formulated as (C) on the basis of the Angeli-Thiele scheme,

(C.) $N\equiv N^{\mp\pm}C<\begin{matrix}CO_2Et\\CH_2\cdot CH_2\cdot CO_2Et\end{matrix}$ $\quad$ $\overset{-}{N}\!=\!\overset{+}{N}\!>C<\begin{matrix}CO_2Et\\CH_2\cdot CH_2\cdot CO_2Et\end{matrix}$ (D.)

which is in better agreement with the modern views of Lewis and Langmuir than is (D) on the Curtius scheme. Further observations by Levene and Mikeska (*J. Biol. Chem.*, 1922, **52**, 485; 1923, **55**, 795) on diethyl diazosuccinate indicate that a compound of the type $N_2{=}C<\begin{matrix}R_1\\R_2\end{matrix}$ can exhibit optical activity, whilst Phillips (J., 1925, **127**, 2552) has described an optically active form of ethyl *p*-toluenesulphinate, $EtO\cdot\overset{+}{S}(\cdot\overset{-}{O})\cdot C_7H_7$. In a recent historical survey (*Die Naturwissenschaften*, 1925, 331) Walden has also directed attention to the asymmetry of the sulphur, selenium, and tin compounds prepared by Pope, and suggests that the sulphur atom in the optically active methylethylthetine ion, $CH_3{>}S{<}\begin{matrix}CH_2\cdot CO_2H\\C_2H_5\end{matrix}$, for example, has an electric charge which plays the part of a group.

Other examples of the application of semipinacolinic deamination for the preparation of optically active ketones are now described. Whereas *d*-alanine gives, by the action of magnesium phenyl bromide on its ester hydrochloride, an amino-alcohol of the opposite

sign of rotation, the amino-alcohol obtained from *d*-phenylalanine by the same method has the same sign of rotation as that of the parent amino-acid, namely, dextrorotatory, and it has the same configuration. The deamination, however, caused a change of sign, *d*-β-amino-αα-diphenyl-β-benzylethyl alcohol giving *l*-benzyldeoxybenzoin:



Thus, whilst dextrorotatory alanine gives dextrorotatory methyldeoxybenzoin, the ketone derived from dextrorotatory phenylalanine is lævorotatory. In a similar manner, *l*-phenylalanine was converted into a lævorotatory amino-alcohol which gave *d*-benzyldeoxybenzoin. The configuration of the *d*- and *l*-benzyldeoxybenzoins in relationship to the parent amino-acids is unknown owing to the possibility of an intramolecular Walden inversion during the deamination of the amino-alcohol.

The optically active ketones described are very readily racemised at the ordinary temperature when a few drops of alcoholic potash are added to their alcoholic solutions. For comparison, the effect of the catalyst on *l*-benzoin is described. The catalytic racemisation of *l*-benzoin was first interpreted by Wren (J., 1909, **95**, 1593) on the basis of a desmotropic change caused by the migration of a hydrogen atom, and on this assumption *d*-methyldeoxybenzoin undergoes racemisation through an enolic complex:

$$d\text{-}\ \begin{matrix}Me\\Ph\end{matrix}\!>\!CH\cdot CO\cdot Ph \longrightarrow \begin{matrix}Me\\Ph\end{matrix}\!>\!C{=}C\!<\!\begin{matrix}OH\\Ph\end{matrix} \longrightarrow r\text{-}\ \begin{matrix}Me\\Ph\end{matrix}\!>\!CH\cdot CO\cdot Ph.$$

Subsequent work by McKenzie and Wren on the hydrolysis of optically active esters by alcoholic potash (compare McKenzie and Smith, *Ber.*, 1925, **58**, 894) and by McKenzie and Smith on the catalytic racemisation of optically active acid amides (J., 1922, **121**, 1348) has provided evidence that the catalyst is potassium ethoxide, and it is suggested that the hypothetical enolic isomeride is formed only after the catalyst has combined with the ester or amide. A similar interpretation can be advanced with regard to ketones like methyldeoxybenzoin which contain (*a*) a phenyl group attached to the asymmetric carbon atom, and also (*b*) a hydrogen

atom attached to the asymmetric carbon atom which in turn is attached directly to a carbonyl group. The point is emphasised that *the latter hydrogen atom has no migrational tendency in the ketone itself, and does not become mobile until an additive complex with potassium ethoxide has first been formed.*

We are continuing our work on semipinacolinic deamination, more particularly with reference to the preparation of optically active ketones derived from phenylaminoacetic acid, phenylalanine and alanine. A few additional observations on the action of magnesium benzyl chloride on *d*-benzyldeoxybenzoin, ethyl *r*-alanine hydrochloride, and ethyl *r*-phenylaminoacetate hydrochloride, respectively, and on the deamination of *r*-β-amino-β-phenyl-αα-dibenzylethyl alcohol are recorded at the end of the experimental section.

Experimental.

Optically Active Methyldeoxybenzoin.

Action of Magnesium Phenyl Bromide on Ethyl d-*Alanine Hydrochloride.*—The final purification of the *d*-alanine employed was effected by dissolving the amino-acid in hot water, and then adding rectified spirit until crystallisation started. The amino-acid separated in long, silky needles, and, for comparison with the value of the specific rotation quoted by Fischer (*Ber.*, 1906, **39**, 464), 0·8000 g. was made up to 10 c.c. with *N*-hydrochloric acid; this solution gave $\alpha_D + 1{\cdot}17°$ in a 1-dcm. tube, whence $[\alpha]_D + 10{\cdot}4°$ for the hydrochloride ($c = 11{\cdot}276$), a value identical with Fischer's.

d-Alanine ethyl ester hydrochloride (15 g., 1 mol.) was added in instalments to an ethereal solution of magnesium phenyl bromide prepared from bromobenzene (150 g., 10 mols.), and the mixture was heated for 5 hours. The additive complex underwent slow decomposition when ice, ammonium chloride, and ammonia were added. When the decomposition was completed, the mixture was extracted several times with ether, the ethereal solution was dried with anhydrous sodium sulphate, the ether was expelled, and the resulting oil recrystallised from light petroleum. The crystals obtained were washed with light petroleum, and then consisted of the optically pure amino-alcohol (5·8 g.). The light petroleum was evaporated from the filtrates, the diphenyl was removed by distillation in steam, and the residual oil was extracted with ether. The oil resulting from the ethereal solution was dissolved in hot aqueous alcohol, and a mixture of oil and crystals separated on cooling. The oil was separated from the crystals by means of light petroleum, and in this manner an additional 5·2 g. of the amino-alcohol were obtained. Total yield = 11 g.

In another preparation the procedure was varied as follows. *d*-Alanine ethyl ester hydrochloride (8 g.) was added gradually to the Grignard reagent prepared from bromobenzene (98 g.), and the mixture after 3 hours' heating was decomposed by ice and dilute hydrochloric acid. In this case the diphenyl remained in the ethereal layer, which was separated from the aqueous layer containing the solution of the hydrochloride of the amino-alcohol. The latter solution was then decomposed by ammonia, but the precipitate which formed contained, not only the free amino-alcohol, but also some of its hydrochloride; the latter was removed by treatment with hot water. Yield of pure amino-alcohol = 4 g. The homogeneity of the amino-alcohol from this and from the preceding preparation was established by repeatedly crystallising from aqueous alcohol and examining the crystals polarimetrically. The amino-alcohol prepared from *d*-alanine is lævorotatory in chloroform, or in ethyl alcohol.

l-β-*Amino-αα-diphenyl*-n-*propyl alcohol*, $CH_3{\cdot}CH(NH_2){\cdot}CPh_2{\cdot}OH$, separates from aqueous alcohol in needles, m. p. 101·5—102·5°. The *r*-isomeride (McKenzie and Wills, *loc. cit.*) also melts at 101·5—102·5°. The *l*-amino-alcohol is very sparingly soluble in water or in light petroleum, and readily soluble in ethyl alcohol, chloroform, benzene, toluene, or acetone (Found: C, 79·1; H, 7·7. $C_{15}H_{17}ON$ requires C, 79·3; H, 7·5%). Its colour reaction with concentrated sulphuric acid is similar to that exhibited by the *r*-isomeride. Its specific rotation was determined in chloroform: $l = 2$, $c = 1{\cdot}6776$, $\alpha_D^{16°} - 2{\cdot}76°$, $[\alpha]_D^{16°} - 82{\cdot}3°$; $\alpha_{5461}^{15·5°} - 3{\cdot}32°$, $[\alpha]_{5461}^{15·5°} - 99{\cdot}0°$. In ethyl alcohol: $l = 2$, $c = 1{\cdot}6628$, $\alpha_D^{16·5°} - 2{\cdot}11°$, $[\alpha]_D^{16·5°} = -63{\cdot}4°$; $\alpha_{5461}^{16·5°} = -2{\cdot}51°$, $[\alpha]_{5461}^{16·5°} - 75{\cdot}5°$.

The Action of Nitrous Acid on l-β-*Amino-αα-diphenyl*-n-*propyl Alcohol*.—A solution of sodium nitrite (2 g.) in water (10 c.c.) was added drop by drop in the course of ¾ hour to 2·2 g. of the amino-alcohol dissolved in 75 c.c. of 25% acetic acid, the temperature being kept at 0° during the addition. The whole was kept at 0° for 5 hours. The oil, which at first separated, crystallised slowly in needles, which were collected, washed with water, and as usual dried in a vacuum over sulphuric acid before a polarimetric determination was made. Yield: 1·9 g. In chloroform: $l = 2$, $c = 2{\cdot}0092$, $\alpha_D^{17°} + 6{\cdot}33°$, $[\alpha]_D^{17°} + 158°$. Thus the lævorotatory amino-alcohol gave a dextrorotatory ketone. After one crystallisation of the product from aqueous alcohol, fine, silky needles were obtained giving the following value in chloroform: $l = 2$, $c = 2{\cdot}0096$, $\alpha_D^{16°} + 7{\cdot}15°$, $[\alpha]_D^{16°} + 178°$. As the substance, however, was not yet optically pure, the deamination of the amino-alcohol was conducted in three additional experiments with 2·5 g., 4·3 g.,

and 5·2 g., respectively. The 9 g. of crude ketone thus obtained were crystallised repeatedly from aqueous alcohol until determinations of the rotatory power showed that the ketone had been obtained pure. Five crystallisations were necessary. Yield = 4 g.

d-*Methyldeoxybenzoin*, $C_6H_5{\cdot}CH(CH_3){\cdot}CO{\cdot}C_6H_5$, crystallises from aqueous alcohol in glistening, silky plates or needles, m. p. 34—35° (Found: C, 85·5; H, 6·7. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%). It is readily soluble in the commoner organic solvents. It gives a pale yellowish-green coloration when a trace is dissolved in cold concentrated sulphuric acid. Determinations of its specific rotation gave the following results. In chloroform for $c = 1{\cdot}0715$ ($l = 2$):

λ	6563	5893	5461	4861	4358
$a^{17°}$	+3·39°	+4·44°	+5·57°	+7·99°	+11·86°
$[\alpha]^{17°}$	+158°	+207°	+260°	+373°	+553°

In ethyl alcohol:

$$l = 2,\ c = 2{\cdot}2320,\ \alpha_D^{18°} + 9{\cdot}41°,\ [\alpha]_D^{18°} + 210{\cdot}8°.$$

After 1 day at the ordinary temperature, the solutions exhibited no autoracemisation.

Optically Active Benzyldeoxybenzoins.

Resolution of r-*Phenylalanine.*—The method of Fischer and Schoeller (*Annalen*, 1907, **357**, 1) was employed. Formyl-*r*-phenylalanine was resolved by brucine in methyl-alcoholic solution, and the resulting *d*- and *l*-formyl-acids were hydrolysed by hydrobromic acid. The *d*-phenylalanine obtained gave in aqueous solution: $l = 2$, $c = 2{\cdot}043$, $\alpha_D^{16°} + 1{\cdot}43°$, $[\alpha]_D^{16°} + 35{\cdot}0°$, whilst the *l*-amino-acid gave in the same solvent: $l = 2$, $c = 2{\cdot}043$, $a_D - 1{\cdot}42°$, $[\alpha]_D - 34{\cdot}8°$. The values quoted by Fischer and Schoeller are: for the *d*-acid, $[\alpha]_D^{20°} + 35{\cdot}14°$, and for the *l*-acid, $[\alpha]_D - 35{\cdot}09°$.

For the preparation of the optically active phenylaminoacetic acids, the resolution of the *r*-acid by Reychler's *d*-camphorsulphonic acid * was in our experience (McKenzie and Wills, *loc. cit.*) more practicable than that described by Fischer and Weichhold (*Ber.*, 1908, **41**, 1286) through the agency of the formyl-*r*-acid. Accordingly, attempts were made to prepare the optically active phenylalanines on similar lines. The homogeneous *d*A*d*B salt was obtained by combining the *r*-amino-acid with an equimolecular quantity of *d*-camphorsulphonic acid, and then crystallising the salt several times until the rotation was constant in value.

d-*Phenylalanine* d-*camphorsulphonate* separates from water in

* Recent work on the constitution of Reychler's acid indicates that the sulphonic group occupies the 10-position in the camphor molecule with sulphonation of the methyl group (Wedekind, Schenk, and Stüsser, *Ber.*, 1923, **56**, 633).

needles. In aqueous solution: $l = 2$, $c = 2{\cdot}0200$, $\alpha_D^{18{\cdot}5°} + 0{\cdot}74°$, $[\alpha]_D^{18{\cdot}5°} + 18{\cdot}3°$. We did not, however, find that this was a convenient method for effecting the resolution. Crystallisation took place too sluggishly, whether effected from water, benzene, aqueous alcohol or aqueous acetone, and the yield of the pure salt was small.

The enantiomorphous salt was prepared by combining *l*-phenylalanine with *l*-camphorsulphonic acid in methyl-alcoholic solution.

l-*Phenylalanine* l-*camphorsulphonate* separates from methyl alcohol in plates, m. p. 109—110°. In aqueous solution: $l = 2$, $c = 2{\cdot}0208$, $\alpha_D^{18{\cdot}5°} - 0{\cdot}74°$, $[\alpha]_D^{18{\cdot}5°} - 18{\cdot}3°$.

The Action of Nitrous Acid on l-β-*Amino-αα-diphenyl-β-benzylethyl Alcohol.*—The *l*-amino-alcohol was prepared by the action of magnesium phenyl bromide on *l*-phenylalanine (compare the preparation of the *d*-amino-alcohol, McKenzie and Wills, *loc. cit.*). The mixture of 1·9 g. of the *l*-amino-alcohol and 40 c.c. of 25% acetic acid was warmed until most of the solid had dissolved, and was then cooled to 0°. The gradual addition of a solution of sodium nitrite (1·3 g. in 10 c.c. of water) during 30 minutes caused the separation of a voluminous solid, which was kept for 4 hours at 0° in contact with the solution. This solid (1·25 g.) was strongly *dextrorotatory*, giving in chloroform solution $[\alpha]_D + 233°$ for $c = 1{\cdot}346$ ($l = 2$). It consisted of the almost pure ketone, and was recrystallised twice from ethyl alcohol.

d-*Benzyldeoxybenzoin*, $CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}Ph$, is sparingly soluble in ethyl alcohol, from which it separates in silky needles, m. p. 121—121·5° (Found: C, 88·3; H, 6·5. $C_{21}H_{18}O$ requires C, 88·1; H, 6·3%). It is readily soluble in chloroform, ether, or acetone. Its specific rotation was determined in chloroform: $l = 2$, $c = 1{\cdot}348$, $\alpha_D^{16°} + 6{\cdot}50°$, $[\alpha]_D^{16°} + 241°$. In ethyl alcohol: $l = 2$, $c = 0{\cdot}392$, $\alpha_D^{16°} + 1{\cdot}90°$.

The Action of Nitrous Acid on d-β-*Amino-αα-diphenyl-β-benzylethyl Alcohol.*—The deamination was conducted as in the preceding case. The crude product (0·8 g.) obtained from the *d*-amino-alcohol (0·9 g.) was strongly *lævorotatory* in chloroform solution, giving $[\alpha]_D - 195°$ for $c = 1{\cdot}5984$ ($l = 2$). It was crystallised thrice from ethyl alcohol until the optically pure ketone was obtained.

l-*Benzyldeoxybenzoin* crystallises from ethyl alcohol in silky needles, m. p. 121—121·5°. With concentrated sulphuric acid, a trace of the compound gives a faint greenish-yellow coloration. The following determinations of the specific rotation were made. In chloroform: $l = 1$, $c = 1{\cdot}258$, $\alpha_D^{16{\cdot}5°} - 3{\cdot}04°$, $[\alpha]_D^{16{\cdot}5°} - 242°$. In acetone: $l = 1$, $c = 1{\cdot}118$, $\alpha_D^{18°} - 2{\cdot}45°$, $[\alpha]_D^{18°} - 219°$; $\alpha_{5461}^{17°} - 3{\cdot}00°$, $[\alpha]_{5461}^{17°} - 268°$.

It is very unusual to find an optically active compound and

its inactive isomeride melting at practically the same temperature. Several such cases have been noted in the course of the present research; thus, *r*-β-amino-αα-diphenyl-β-benzylethyl alcohol melts at 144·5—145·5° (McKenzie and Richardson, J., 1923, **123**, 91), whereas the *d*-isomeride melts at 143—144° (McKenzie and Wills, *loc. cit.*, p. 293). *r*-Benzyldeoxybenzoin melts at 121·5—122° (McKenzie and Richardson, *loc. cit.*; McKenzie and Roger, J., 1924, **125**, 849), whereas the optically active isomerides melt at 121—121·5°, and reference has been already made to *l*- and *r*-β-amino-αα-diphenyl-*n*-propyl alcohols, which melt at 101·5—102·5°.

Catalytic Racemisation of Optically Active Ketones.

l-*Benzoin*.—This ketone was prepared by the action of magnesium phenyl bromide on *l*-mandelamide (McKenzie and Wren, J., 1908, **93**, 309). A determination was made of its specific rotation in ethyl-alcoholic solution: $l = 2$, $c = 1{\cdot}1550$, $\alpha_D^{16°} - 3{\cdot}06°$, $[\alpha]_D^{16°} - 132{\cdot}5°$. To this solution in a 2-dcm. tube, four drops of ethyl-alcoholic potash (0·4487*N*) were added, and quickly mixed. Polarimetric readings were taken at intervals, and after 1 hour three additional drops of the alcoholic alkali were added. The initial reading immediately after the addition of the alkali was $\alpha_D - 3{\cdot}05°$; t = interval (minutes) after addition of the catalyst, and $\theta°$ = observed angle:

t	15	30	45	60	65	80	100	120	140
$\theta°$	−2·77	−2·68	−2·61	−2·61	−2·49	−2·26	−2·00	−1·82	−1·72
t	180	220	250	280	340	400	23 hrs.	31 hrs.	5 days
$\theta°$	−1·48	−1·22	−1·06	−0·91	−0·70	−0·55	−0·24	−0·22	−0·22

d-*Methyldeoxybenzoin*.—An ethyl-alcoholic solution of the ketone ($c = 0{\cdot}8095$) gave $\alpha_D^{16°} + 3{\cdot}37°$ in a 2-dcm. tube. Four drops of ethyl-alcoholic potash (0·4487*N*) were mixed with the solution, and the fall in rotation was noted as below:

t (mins.)	1	10	20	30	40	50	60	90
$\theta°$	+3·36	+3·25	+3·13	+3·04	+2·94	+2·83	+2·74	+2·54
t (hours)	2	3	4	5	6	7	7½	23½	29½	47½
$\theta°$	+2·32	+2·00	+1·70	+1·49	+1·25	+1·04	+0·94	+0·10	+0·07	+0·00

The alcohol was evaporated from the solution, and the solid was crystallised from ethyl alcohol; silky needles of *r*-methyldeoxybenzoin, m. p. 49·5—50·5°, separated.

d-*Benzyldeoxybenzoin*.—An ethyl-alcoholic solution of the ketone ($c = 0{\cdot}392$) gave $\alpha_D^{16°} + 1{\cdot}90°$ in a 2-dcm. tube, and this value was unchanged after 1 day at the ordinary temperature. Three drops (0·05 c.c.) of ethyl-alcoholic potash (0·4487*N*) were then mixed with the solution and the fall in rotation was noted as below:

t.	*θ.*	*t.*	*θ.*	*t*	*θ.*
1 min.	+1·87°	4 hours	+1·26°	24 hours	+0·31°
10 „	1·82	5 „	1·15	26 „	0·25
20 „	1·78	6 „	1·05	32 „	0·16
30 „	1·74	7 „	0·96	48 „	0·06
1 hour	1·63	8 „	0·88	54 „	0·05
2 hours	1·49	11 „	0·74	73 „	0·02
3 „	1·37	12 „	0·69		

Action of Magnesium Benzyl Chloride on d-*Benzyldeoxybenzoin.*—The mixture of the ketone (0·6 g.) and the Grignard reagent prepared from benzyl chloride (2 g.) was boiled for 6 hours and then decomposed by ice and dilute sulphuric acid. The ethereal layer was dried, the ether expelled, and the oil triturated with hot light petroleum. The resulting solid was crystallised from light petroleum (b. p. 80—100°), d-αβ-*diphenyl*-αβ-*dibenzylethyl alcohol*, $CH_2Ph{\cdot}CHPh{\cdot}CPh(OH){\cdot}CH_2Ph$, separating in rosettes of needles, m. p. 167—168° (Found: C, 88·6; H, 7·0. $C_{28}H_{26}O$ requires C, 88·8; H, 6·9%). In chloroform: $l = 1$, $c = 1{\cdot}306$, $\alpha_D^{17°} + 2{\cdot}02°$, $[\alpha]_D^{17°} + 155°$.

We are indebted to Mr. Arthur Kelman Mills for the following observations.

Action of Magnesium Benzyl Chloride on Ethyl r-*Alanine Hydrochloride.*—The ester hydrochloride (1 mol.) was heated for several hours with the Grignard reagent prepared from benzyl chloride (9 mols.). The mixture was decomposed by ice and ammonium chloride, the ether layer separated, the ether expelled, and the dibenzyl removed by steam distillation. The product was purified by crystallising first from light petroleum and then from rectified spirit.

r-β-*Amino*-αα-*dibenzyl*-n-*propyl alcohol*,

$$(PhCH_2)_2C(OH){\cdot}CHMe{\cdot}NH_2,$$

is moderately soluble in rectified spirit, from which it crystallises in plates, m. p. 93·5—94·5° (Found: C, 80·1; H, 8·4. $C_{17}H_{21}ON$ requires C, 80·0; H, 8·3%).

Action of Magnesium Benzyl Chloride on Ethyl r-*Phenylaminoacetate Hydrochloride.*—The ester hydrochloride (10 g., 1 mol.) was added to the Grignard reagent prepared from benzyl chloride (52·5 g., 9 mols.) and boiled for 3 hours. After decomposition with ice and ammonium chloride, the ethereal layer was separated and dried and from it an oil was obtained which was dissolved in hot light petroleum (b. p. 60—80°). 6·9 G. of solid crude amino-alcohol separated. This was recrystallised from rectified spirit; 6·0 g. of β-amino-αα-dibenzyl-β-phenylethyl alcohol, m. p. 125—126°, were then obtained. This compound has already been described by Thomas and Bettzieche (*Z. physiol. Chem.*, 1924, **140**, 244), who used somewhat different experimental conditions from the above.

Deamination of r-β-*Amino*-β-*phenyl*-αα-*dibenzylethyl Alcohol.*—To the solution of the amino-alcohol (4 g.) in 25% acetic acid (120 c.c.) an aqueous solution of sodium nitrite (3 g.) was added while the whole was maintained at 0°. The white solid which at first separated soon became viscous, and was extracted with ether. The product from the ethereal solution was dissolved in alcohol, and the solid which separated was crystallised twice from light petroleum (b. p. 40—60°). The resulting rosettes of needles consisted of benzyl αβ-diphenylethyl ketone, $CH_2Ph{\cdot}CHPh{\cdot}CO{\cdot}CH_2Ph$, m. p. 74—75°. For comparison, α-phenyl-ββ-dibenzylethylene glycol was prepared from ethyl *dl*-mandelate by the action of magnesium benzyl chloride, and dehydrated with concentrated sulphuric acid according to Orékhov (*Bull. Soc. chim.*, 1919, **25**, 111). When prepared in the latter manner, the ketone had m. p. 74—75° (Orékhov gives 75—76°), and there was no depression of the melting point when it was mixed with the product of the deamination.

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CVII.—*Experiments on the Variation of the Angles of Crystals during Growth.*

By ERNEST SYDNEY HEDGES.

THE slight deviations from the theoretical angle which are to be observed in almost every crystal and the replacement of a theoretical face by a series of faces inclined to each other at minute angles are familiar to everyone who has carried out accurate measurements with a goniometer. In the practical measurement of these crystals it is customary to take the mean of such a set of readings, and in the majority of cases the method produces good results from a theoretical point of view. These vicinal faces are generally ignored, therefore, in determining the symmetry of the crystal. A study of the actual process of crystallisation, however, is incomplete if these forms are left neglected; in fact, regarded from a purely physical point of view, the existence of such faces may be a matter of some importance, and one which may help towards the elucidation of the process of crystallisation.

Several investigators have been interested in these variations and

have made exhaustive measurements on crystals which have been removed from the mother-liquor. Pfaff (*Sitzungsber. Physik. Med. Erlangen*, 1878, **10**, 59), from a study of cubic crystals, concluded that the variations were exhibited by birefringent specimens, indicating a state of strain. Brauns (*Neues Jahrbuch*, 1887, **1**, 136) could not confirm this opinion, and experiments with lead nitrate led him to suggest that the vicinal faces are really faces of low indices which have been distorted under the influence of gravity. Wulff (*Z. Kryst. Min.*, 1901, **34**, 449) supposed the variations to be due to concentration currents playing over the crystal during its growth.

In order to study this problem more fully, a special type of goniometer was devised by Miers (*Phil. Trans.*, 1903, A, **202**, 459), which permitted of the measurement of a crystal *during its growth*. The observations were concerned mainly with potassium alum and ammonium alum, and it was shown that the octahedral planes are invariably replaced by vicinal faces belonging to triakis octahedra which are subject to continual variations during the growth of the crystal.

The experiments described in the present paper are a continuation of this work, which the author has undertaken at the suggestion of Sir Henry Miers, using the same goniometer. The observations have been made over the course of the last three years and the work had to be discontinued abruptly. It is thought that the results so far achieved, although incomplete, may prove of interest and value.

Experimental.

Orthorhombic System.—For the purpose of studying the variations of angle exhibited by the vicinal faces during crystallisation, the crystal was immersed in a slightly supersaturated solution made up at a few degrees above room temperature and readings were taken at various time intervals for several hours. As a rule, immediately after immersion the images yielded by the vicinal faces became poor owing to a slight dissolution of the crystal. Crystallisation began quickly at first and subsequently became slower as the temperature of the solution approximated to that of the room. The substances used were sodium potassium tartrate and magnesium sulphate.

Two important results were derived from these experiments. (1) During the growth of a crystal the number of vicinal faces increases at first, generally reaching a maximum about one hour after immersion, after which the number of images steadily diminishes.

This process runs parallel with the rate of crystallisation, which increases to a maximum during the initial cooling and then slows

down as the crystallising temperature reaches that of the room. The following series of measurements, giving the readings for images from the vicinal faces occurring in a fixed portion of the prism zone of sodium potassium tartrate, illustrates this point. All columns of figures are to be read vertically.

TABLE I.

2.30 p.m.	2.45 p.m.	3.00 p.m.	3.15 p.m.	4.25 p.m.
269° 42½′	270° 10′	269° 55½′	270° 0′	272° 26½′	271° 2′
270 10	271 4½	270 5½	270 7½ (A)	272 31	271 10
272 35	271 14	271 8	270 15	272 40	272 24
	271 22	271 23½	270 57		272 47
	272 10	271 59	271 24		
		272 27	272 0		
		272 35	272 17		

This series of results is representative of the behaviour observed with nine crystals of sodium potassium tartrate. Similarly, Table II shows the total number of faces in the prism zone of magnesium sulphate yielding definite images at various times during the growth of a crystal, and is characteristic of the general results obtained with numerous other crystals.

TABLE II.

Time	1·25 p.m.	1·45 p.m.	2·10 p.m.	2·45 p.m.
No. of faces	9	13	16	11

(2) During the process of growth, the positions of the faces undergo rapid variations of considerable magnitude.

A rather extreme case was observed with the face marked A in Table I—an image chosen on account of its peculiar brightness. The image was kept under continuous observation for an hour and its position was read every minute. The readings vary in a very irregular fashion, the highest being 270° 10′ and the lowest 269° 50′. The variation here is unusually large for an individual image, and this may correspond with the very rapid growth of the crystal which was observed in this particular experiment. The next series of readings, taken at five-minute intervals on a different crystal, is more characteristic of a general case: 205° 22′, 205° 20′, 205° 20½′, 205° 19½′, 205° 20′, 205° 20½′, 205° 20′.

An idea of the individual variations in the positions of the faces in the case of magnesium sulphate is gained from the following values for two bright images taken during growth. This example has been selected from series of readings taken with eleven different crystals of magnesium sulphate at various times.

4.40 p.m.	5.35 p.m.	6.15 p.m.
264° 7½′	264° 11½′	264° 14′
264 16	264 13½	264 16½

Tetragonal System.—A few experiments carried out with di-ammonium hydrogen phosphate confirmed the same general results. The faces on these crystals belong to two forms—prism and pyramid—and according to Groth no other forms have been observed. Both forms were found to be replaced by vicinal faces and the measurements of the prism zone given in Table III show that there is a maximum deviation of 20′ from the right angle.

TABLE III.

2.40 p.m.				3.10 p.m.				3.35 p.m.			
118°	38′	298°	36′	118°	37½′	298°	41′	118°	36′	298°	34′
		298	33	118	36	298	35				
208	37	28	34	208	35	28	34	208	33	28	34
						28	20			28	20

Cubic System.—More detailed experiments were conducted with sodium chlorate. Initially, the method was the same as in the foregoing case, *i.e.*, the measurements were taken over the course of a few hours during the slow cooling of a solution. Under such conditions, the crystal is never in equilibrium with the mother-liquor. It is necessary to reproduce only one set of readings to represent the general results observed with nineteen crystals which have been examined.

Table IV records the complex images replacing the cube faces of a dextrorotatory sodium chlorate crystal. In addition to the exact position in the horizontal plane, the direction of those images which are out of the horizontal zone is indicated, although for the present purpose the distance above or below the zone was not measured.

TABLE IV.

1.45 p.m.			2.15 p.m.			2.45 p.m.			3.20 p.m.		
192°	27′		192°	27′	Below.	192°	28′	Below.	192°	28′	Below.
192	33		192	33½	Below.	192	45½	,,	192	30	,,
192	48½		193	1½	Two vert., v. bright.	192	59	On.	192	43	On.
193	1½	V. bright.				193	0	V. bright.	192	54	,,
193	3					193	2		192	59	Two vert.
282	37		282	37½		282	37½		282	39	
282	46	Below.	282	40		282	40		282	48	
282	54		282	45	Below.	282	52½	Two vert.	282	51	V. bright
282	58	Above.	282	51							
			282	54	V. bright.						
			282	56							
12	31		12	30		12	30		12	29	
12	37		12	36		13	0	Bright. Sl. above.	12	35	
12	57		12	56					12	58	Above, v. bright.
13	1		13	0	Sl. above and v. bright.	13	1½				
13	3	V. bright.	13	2							
13	5										
102	40	Above.	102	36	Above.	102	43	Above.	102	43	Above.
102	43	Three vert.	102	39	,,	102	47	,,	102	47	,,
102	46	Above.	102	43	,,	102	52	On.	102	51	On.
102	55	Two vert.	102	46	,,	102	54	Below.	102	53	Below.
			102	53	On.						
			102	57	Above.						

In this case, the mean of the vicinal faces *in the horizontal zone* replacing the cube face is calculated, and Table V, where these values are grouped, indicates that it is impossible to ascertain the true position of the cube faces by taking the mean of such readings.

TABLE V.

Mean Positions.

Time.	A.	B.	C.	D.
1·45 p.m.	192° 45½′	282° 45½′	12° 52′	102° 49′
2.15 „	193 1½	282 48	12 35	102 53
2.45 „	193 0$\bar{1}$	282 57	12 46	102 52
3.20 „	192 57	282 44½	12 32	102 51

Suggested Cube Faces.

1.45 „	193 1½	282 54	13 1	102 55
2.15 „	193 1½	282 54	13 1	102 53
2.45 „	193 0	282 52½	13 0	102 52
3.20 „	192 59	282 51	12 58	102 51

The table also gives the readings which would correspond to the cube faces on the assumption that the vicinal faces in accordance with the symmetry of the crystal belong to forms {*hko*} in a horizontal zone on one face and {*okl*} in a vertical zone on the adjacent face. The suggested cube face is the point of intersection of a vertical zone with a horizontal zone. The validity of the assumption is shown later. For example, at 2·15 p.m., the reading 193° 1½′ represents an image in the horizontal plane which is duplicated in the vertical plane, and an examination of the tables shows that this face is prominent throughout the growth. Parallel to this face there occur the readings 13° 0′ and 13° 2′ arranged symmetrically about the suggested cube face, and inspection shows these faces to be prominent throughout. On the other hand, at right angles to these faces there is nothing to correspond. If the probable positions of the other pair of cube faces are worked out by the same method, they have a mean value of 282° 53′ and 192° 53′.

The Vicinal Faces in Relation to the Symmetry.—The symmetry of sodium chlorate is the lowest type of the cubic system. There are no planes of symmetry, but there is a threefold axis passing through each solid angle of the cube and a two-fold axis normal to each cube face. If, therefore, the vicinal faces belong to the form {*hko*} and are consistent with the symmetry of the crystal, one would expect the vicinal faces replacing each pair of opposite cube planes to be disposed alike and to differ from the other pair in a perpendicular sense. This has been found to occur without exception in every crystal of sodium chlorate examined. In the cube faces A and C, the images are arranged mainly in the horizontal zone and in faces B and D they occur for the most part in a vertical zone.

Additional evidence on this point is observed when the crystal

is first immersed or during the incipient stages of dissolution when the temperature of the room rises. Under such conditions, a narrow band or haze of light appears in the field which represents either a rounded surface or a continuous series of facets etched on the crystal by the solvent. On one pair of parallel faces this band lies in the horizontal plane and on the other pair it is vertical. Conditions are often realised when such a vertical band is present simultaneously with well-developed images occurring either in the band or in the horizontal zone. This condition permits of a more certain way of determining the positions of the true cube faces, which is applicable even when the cube faces are themselves absent. Accurate measurements of sharp images appearing in the horizontal and vertical bands can be made and the point of intersection of the zones may be taken as the theoretical position of the cube face.

FIG. 1.

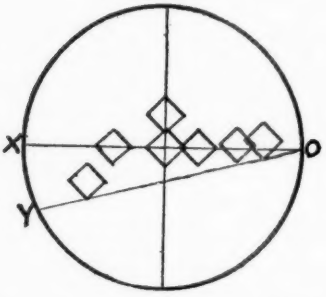
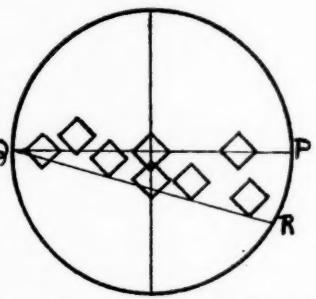


FIG. 2.



Thus, in one crystal, the positions of the vertical bands yielded by the faces B and D were measured as 104° 10′ and 284° 10′, respectively. The true cube faces may be taken, therefore, as 14° 10′, 104° 10′, 194° 10′, 284° 10′. The images actually yielded by the faces A and C were: A = 13° 54′, 14° 4′, 14° 20′; C = 194° 0′, 194° 20′. Although the cube faces are here not present, they are replaced by faces inclined symmetrically on either side.

The images, however, are not confined solely to the horizontal plane or to the vertical plane, and several occur which do not belong to either zone. Fig. 1 represents the appearance of the field in viewing the horizontally disposed face of a dextrorotatory crystal of sodium chlorate and may be compared with Fig. 2, which represents a similar state in a lævorotatory crystal.

Attention may be directed to the upward trend from left to right in the faces A and C of the right-handed crystal and the downward trend from left to right in the corresponding faces of the left-handed crystal. Similarly, the trend of faces B and D was in the opposite direction in the two enantiomorphs. The angles *XOY* and *PQR*

were measured as 16° and 17°, respectively. This effect was noticed in two other specimens (right- and left-handed, respectively) which originated in the same batch of crystals. In later experiments, however, such a differentiation between the optical isomerides was not observed. No cases have appeared where the disposition is in an opposite sense to this, but those images which do not belong to either zone have been arranged in an apparently haphazard way.

Thus, although it is not possible to deduce the direction of optical rotation from the disposition of the vicinal faces, there is a tendency for these to be arranged in accordance with the optical properties of the crystal.

Experiments on Slow Growth.—With the object of studying the forms produced when the crystal is in true equilibrium with the solution, a crystal of sodium chlorate was induced to grow very slowly over a period of several weeks and readings were taken every morning about 9.30 a.m. before the room had warmed up. To realise favourable conditions for such experiments was a matter of considerable difficulty and in the damp Manchester atmosphere it was only found possible during the summer months; at other times of the year, the saturated solution tended to gain water often. When the necessary climatic conditions prevailed, the method adopted was to place a glass cover over the whole instrument during the night, when the crystal grew mainly by cooling, and to remove it during the day, when the crystal grew mainly by evaporation. In this way, crystallisation was always slow and a crystal did not increase in breadth by more than a quarter of an inch in a month.

The arrangement of the images during the first stages of slow growth was precisely similar to that already described, during the rapid growth of sodium chlorate crystals, the complex faces A and C differing in a perpendicular sense from the faces B and D. Again, the total number of images present underwent a progressive decrease with time. In addition to this, however, there was observed a most marked flattening of the forms during the process—that is to say, the images gradually approached one another until finally what appeared to be a single perfect cube face remained.

To take an example, a crystal was immersed on May 30th, 1924, and Table VI shows the horizontal extent of the complex face A (*i.e.*, the difference in minutes between the extreme images) on successive dates.

TABLE VI.

Date.	Extent.	Date.	Extent.	Date.	Extent.
May 30th	43½′	June 4th	7½′	June 16th	0
June 1st	37	,, 5th	9	,, 18th	0
,, 2nd	8½	,, 9th	14	,, 20th	0
,, 3rd	9	,, 12th	2½	,, 23rd	19′
				,, 30th	8½

The readings 0 for June 16th, 18th, and 20th indicate that on those days there was a single image in the field. An unusual spell of sunny weather over the week-end June 20th—23rd, during which the glass cover was left on, caused a partial dissolution of the crystal, so that the process takes a new start from that date.

Further, during slow growth, the forms flatten with time in both the horizontal and vertical zones, so that the four faces tend to become alike. The case was never realised where the crystal consists of four perfect cube faces existing simultaneously, although there seems to be no doubt that such a state may be arrived at under favourable conditions. Crystals have been observed where at different times each of the four faces in the zone has yielded an image corresponding to a true cube face. As a rule, only one pair of faces would give a single image in the theoretical place of the cube and the other pair would give duplicate images arranged symmetrically. For instance, a crystal after growing for a period of 24 days gave perfect single images at 195° 50′ and 15° 50′ and images of equal intensity arranged symmetrically at 285° 49′, 285° 51′, and 105° 49′, 105° 51′. The following morning, at 195° 50′ and at 15° 50′ there were duplicate images placed one minute above and below the zone, respectively. It is difficult to conceive of a more faithful representation of the symmetry of sodium chlorate.

The Movement of the Faces.—Evidence has been given of the continual variation in the positions of the images, and this point has received comment by Miers (*loc. cit.*), who stated that with potash alum the faces replaced each other *per saltum* in accordance with the law of rational indices. Throughout the present experiments, this has been the case with sodium chlorate and also with ammonium phosphate.

On the other hand, with magnesium sulphate, and particularly with sodium potassium tartrate, two kinds of movement have been observed: not only do the images move by successive replacement, but certain of the images were observed to travel across the field in a continuous manner. This motion was quite rapid, the path generally being about five to ten minutes of arc traversed in about one second of time. The most usual form in which the movement was manifested was when two bright faces occurred on the crystal close together; there was often a continuous migration of less bright but perfectly definite images from one to the other, the rate being of the order of one every few seconds. In some instances, an image was observed to leave a relatively fixed face, move out some distance, and then return. The latter fact seems to remove any doubt as to whether the movements may be a spurious effect due to the optical deflection of an image by currents of solution of

varying refractive index. Such deviations do undoubtedly occur, particularly if the solution is gently stirred, but are in the nature of a quick tremor of relatively small displacement during which the outline of the image becomes indefinite.

Theoretical.

As an explanation of vicinal faces Miers has suggested that the density of packing of molecules in a crystal is considerably greater than the density of packing in the saturated solution and that the molecules of solute, as they separate out of the crystallising solution, cannot squeeze themselves into the very close packing of a face with simple indices. On the other hand, the reticular density of a face inclined at an angle of a few minutes to one of the principal planes of the crystal is very low and much more suitable for the deposition of new units of the structure.

Some of the experiments which have been described above lend additional support to this view, for it is found that the crystal approximates more and more closely to the ideal form the slower the rate of growth. In fact, by carefully controlling the slow growth of sodium chlorate, single true cube faces may be obtained although these faces are generally absent in the ordinary way. Under such conditions of growth, it seems reasonable that the molecules of solute can easily take their places in a plane of high density.

Summary.

Measurements of the vicinal faces in crystals of sodium potassium tartrate, magnesium sulphate, diammonium hydrogen phosphate, and sodium chlorate, taken during the actual growth of the crystal, show that the number of faces undergoes an initial increase with time followed by a decline. The images undergo continual and rapid variations in position, generally by replacement, but in certain cases by continuous progression. The vicinal faces in sodium chlorate are consistent with the symmetry of the crystal, and a method is devised which enables the true positions of the ideal cube faces to be found even when they are absent. The slower the growth of the crystal, the more closely does it approximate to the ideal form. By carefully controlling the slow growth of sodium chlorate, single perfect cube faces may be developed. The experiments support the views of Miers on the cause of vicinal faces.

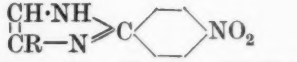
In conclusion, the author wishes to express his cordial thanks to Sir Henry A. Miers, F.R.S., for the constant encouragement and advice which he has received from him throughout the course of this work.

THE UNIVERSITY, MANCHESTER. [*Received, January 14th,* 1926.]

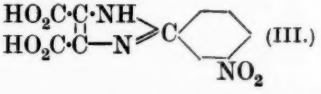
CVIII.—*The Nitration of Benzamidines.*

By Robert Forsyth, Vishvanath Krishna Nimkar, and Frank Lee Pyman.

Pyman and Stanley (J., 1924, **125**, 2484) showed that nitration of 2-phenylglyoxaline and its 4(5)-monocarboxylic acid gave mainly the *p*-nitro-compounds (I and II), whereas 2-phenylglyoxaline-4 : 5-dicarboxylic acid gave mainly the *m*-nitro-compound (III).



(I, R = H. II, R = CO_2H.)

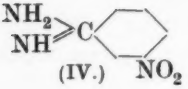


(III.)

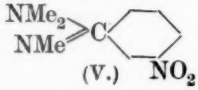
In view of the fact that 2-phenylglyoxaline and its monocarboxylic acid yield salts with mineral acids whereas its dicarboxylic acid does not, they suggested that the different character of the doubly-linked nitrogen atom, that is, the nitrogen atom which takes part in salt formation (compare Burtles and Pyman, J., 1923, **123**, 361), was responsible for the different results. In 2-phenylglyoxaline, this nitrogen atom would be regarded as saturated or positive by combination with acid according as to whether the hypotheses of Flürscheim or Lapworth were employed, whilst in the dicarboxylic acid it would be regarded as unsaturated or negative.

If this explanation were correct, then one would expect that nitration of benzamidine by the method employed for 2-phenylglyoxaline, that is, addition of the nitrate of the base to sulphuric acid, would yield mainly the *o*- and *p*-nitro-compounds, but as a matter of fact it proves to give more than 90% of *m*-nitrobenzamidine (IV).

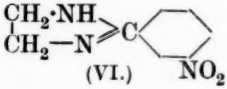
Various possible explanations of the essentially different results of nitrating 2-phenylglyoxaline and benzamidine have now been examined. It might be suggested that since glyoxalines do not readily yield acyl derivatives, we should not postulate nitroamine formation in this case, but might reasonably do so in the case of benzamidines. An explanation would then be furnished analogous to that devised by Holmes and Ingold (J., 1925, **127**, 1800) to explain the difference between the results of nitrating secondary and tertiary benzylamines. Such an explanation, however, was found to be inapplicable in our case, since the nitration of benzenyltrimethylamidine, which cannot yield a nitroamine, gave more than 80% of m-*nitrobenzenyltrimethylamidine* (V).



(IV.)



(V.)



(VI.)

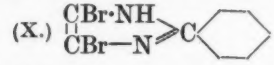
Next, it might be thought that the different results of nitrating 2-phenylglyoxaline and benzamidine might be due to the fact that the two nitrogen atoms were linked together by a closed chain in the former compound and might neutralise each other's influence. This view was disproved by the nitration of 2-phenyl-4 : 5-dihydroglyoxaline, which gave more than 80% of 2-m-*nitrophenyl*-4 : 5-*dihydroglyoxaline* (VI).

It seems to us that the noteworthy difference between the results of nitrating 2-phenylglyoxaline and its dihydro-derivative are probably associated with the fact that glyoxalines have aromatic character whereas their dihydro-derivatives have not. It thus appears that the amidinium ion, $\left[\cdot C\lessdot^{NHR}_{NR'R''}\right]^{\cdot}$, which is contained in the salts of benzamidine, benzenyltrimethylamidine, and 2-phenyl-4 : 5-dihydroglyoxaline, is strongly meta-directive, the nitrogen atoms exerting a similar influence to that of the oxygen atom in the carboxyl group. In the basic 2-phenylglyoxalines, the influence of the nitrogen atoms is suppressed, and the glyoxalinium ion produces an *op*-directive effect, due to the aromatic complex as a whole, and similar to that of phenyl in directing the *p*-nitration of diphenyl. The exceptional predominant *m*-nitration of the non-basic 2-phenylglyoxaline-4 : 5-dicarboxylic acid may be due possibly to the absence of salt formation in the case of this compound, and a difference in orienting properties between glyoxaline bases and glyoxalinium ions, for evidence of a difference in structure between glyoxalines and their salts may be found in the existence of the two isomeric bases 2 : 4- and 2 : 5-diphenylglyoxalines (VII and VIII), which yield a common ion (IX) (Burtles and Pyman, *loc. cit.*).

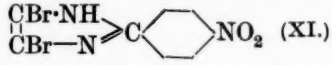
$$\underset{\text{(VII.)}}{\begin{matrix}CH\cdot NH\\ \|\\ CPh-N\end{matrix}\!\!>CPh} \longrightarrow \underset{\text{(IX.)}}{\left[\begin{matrix}CH-NH\\ \|\\ CPh\cdot NH\end{matrix}\!\!>CPh\right]^{\cdot}} \longleftarrow \underset{\text{(VIII.)}}{\begin{matrix}CPh\cdot NH\\ \|\\ CH-\!\!-N\end{matrix}\!\!>CPh}$$

Nevertheless, the fact that the dicarboxylic acid yields 52% of the *m*- with 19% of the *p*-nitro-compound, whilst the monocarboxylic acid yields 52% of the *p*- with 19% of the *m*-compound, shows that the introduction of carboxyl groups into the glyoxaline nucleus of 2-phenylglyoxaline progressively diminishes the ratio of para- to meta-nitration of the benzene nucleus, and suggests, as an alternative explanation, for which we are indebted to Dr. King, that the results should be ascribed to the accumulation of acidic groups attached to the glyoxaline nucleus. In this sense, they are comparable with the results of nitrating benzyl chloride, benzylidene chloride, and benzotrichloride, where also the ratio of para- to meta-nitration is progressively diminished by the introduction of acidic groups

(Holleman, *Rec. trav. chim.*, 1914, **33**, 1). On the other hand, we found no support of this explanation, possibly owing to experimental difficulties, on the nitration of 4 : 5-*dibromo*-2-*phenylglyoxaline* (X),



(X.)



(XI.)

which might be expected to yield a considerable proportion of the *m*-nitro-derivative, for here 4 : 5-*dibromo*-2-p-*nitrophenylglyoxaline* (XI) was isolated in a yield of 63% together with only 1·8% of an unidentified isomeride.

Nitration of 4(5)-*bromo*-2-*phenylglyoxaline* prepared by the reduction of the dibromo-compound with sodium sulphite proceeded less uniformly, possibly owing to nitration of the glyoxaline nucleus, but here the only product isolated was again the para-isomeride, 4(5)-*bromo*-2-p-*nitrophenylglyoxaline*. Another instance of the *p*-directive effect of the glyoxaline nucleus has been recorded by Tröger and Thomas (*J. pr. Chem.*, 1925, **110**, 42), who find that the nitration of lophine gives 2 : 4 : 5-tri-*p*-nitrophenylglyoxaline. Para-nitration of phenyl groups attached to the 2-position of glyoxalines having basic character thus seems to be the rule.

Experimental.

Nitration of Benzamidine.—Benzamidine nitrate,* prepared from the base and dilute nitric acid, crystallised from alcohol in large, colourless, rhombic prisms, m. p. 128° (corr.) after softening from 124°, which are anhydrous and very easily soluble in water or hot alcohol (Found : C, 45·7, 45·6; H, 4·9, 5·0. $C_7H_8N_2,HNO_3$ requires C, 45·9; H, 4·9%). This salt (10 g.) was added gradually to concentrated sulphuric acid (20 c.c.) cooled in ice and salt. After ½ hour, the solution was heated for 2 hours at 100°, then diluted and mixed with aqueous solutions of barium hydroxide (50 g., hydrated) and barium chloride (46·7 g., hydrated). After removing barium sulphate, the aqueous solution was evaporated to dryness under diminished pressure, and the residue crystallised fractionally from alcohol, when 10·1 g. of pure *m*-nitrobenzamidine hydrochloride were isolated, that is, 91·7%.† The salts remaining in the mother-liquors were hydrolysed by boiling with 40 c.c. of 17% aqueous sodium hydroxide until ammonia was no longer evolved. On addition of concentrated hydrochloric acid, 0·62 g. of *m*-nitrobenzoic acid (m. p. 135°) separated, whilst ether collected a further 0·08 g. of less pure material (m. p. 118—120°). Mixtures of

* This salt has not been described previously. The reference to it (*Jahresber.*, 1888, 1133) quoted by Beilstein is a mistake, and applies to the nitrite.

† All yields are expressed in percentage of the theoretical.

these products with pure *m*-nitrobenzoic acid melted at 137° and 126—131°, respectively. The amount of these crops represents 7·8% of the theoretical yield, making in all 99·5%, whence it is clear that the nitration of benzamidine yields almost wholly the meta-isomeride.

m-*Nitrobenzamidine hydrochloride* crystallises from alcohol in clusters of cream-coloured, prismatic needles, m. p. 251° (corr.) after sintering from 248°. It is anhydrous and readily soluble in water or hot alcohol (Found: C, 41·9; H, 4·0; Cl, 17·6. Calc., C, 41·7; H, 4·0; Cl, 17·6%). Tafel and Enoch (*Ber.*, 1890, **23**, 1552), who prepared this salt by the interaction of the hydrochloride of *m*-nitrobenziminoethyl ether with ammonia, give m. p. 240°. The identity and purity of our preparation were established by hydrolysing the salt (1 g.) with 8·5% aqueous sodium hydroxide (40 c.c.), and adding concentrated hydrochloric acid, when 0·564 g. of *m*-nitrobenzoic acid, m. p. 140° (corr.), separated, and 0·25 g., m. p. 139°, was collected by ether, the total yield being 98·2%. The identity of these crops with *m*-nitrobenzoic acid was established by the mixed-melting point method. The first crop was also analysed (Found: C, 50·3; H, 3·0. Calc., C, 50·3; H, 3·0%).

Nitration of Benzenyltrimethylamidine.—Benzenyltrimethylamidine nitrate was prepared by the double decomposition of aqueous solutions of silver nitrate and the corresponding hydriodide, previously called dimethylamidobenzenylmethylimidine hydriodide (Pyman, J., 1923, **123**, 3372). It crystallises from alcohol in large, colourless, prismatic rods, m. p. 195—196° (corr.). It is anhydrous and readily soluble in water or hot alcohol (Found: C, 53·2; H, 6·5; N, 18·5. $C_{10}H_{14}N_2,HNO_3$ requires C, 53·3; H, 6·7; N, 18·7%). This salt (10 g.) was added gradually to concentrated sulphuric acid cooled in ice and salt. The solution was kept for 1 hour at the room temperature, heated for 2 hours at 100°, diluted with water, and mixed with aqueous solutions of barium hydroxide (50 g., hydrated) and barium chloride (46·7 g., hydrated). After removing barium sulphate, the aqueous solution was evaporated to dryness under diminished pressure, when a pale yellow syrup was obtained. Since the hydrochlorides showed little tendency to crystallise, the syrup was diluted and mixed with excess of aqueous sodium iodide, when the hydriodides separated as an oil which soon solidified. After numerous crystallisations from alcohol, using sulphur dioxide as a decolorising agent, 11·01 g. of pure *m*-nitrobenzenyltrimethylamidine hydriodide were isolated (yield 73·9%). The substance remaining in the mother-liquors was hydrolysed with aqueous sodium hydroxide; strong hydrochloric acid then precipitated 0·69 g. of *m*-nitrobenzoic acid, m. p. 133—137°. The filtrate was unfortunately lost.

On recrystallising the acid, 0·52 g. was obtained pure (m. p. 140°) and a further 0·164 g., m. p. 138°. They were identified as *m*-nitrobenzoic acid by the mixed-melting point method. The amount of these crops represents 9·3% of the theoretical yield, making in all 83·2%.

m-*Nitrobenzenyltrimethylamidine hydriodide* crystallises from alcohol in pale lemon-yellow needles, m. p. 243—246° (corr.; decomp.). It is anhydrous, and sparingly soluble in water or cold alcohol, but readily soluble in acetone (Found : C, 35·8; H, 4·1; I, 37·9. $C_{10}H_{13}O_2N_3,HI$ requires C, 35·8; H, 4·2; I, 37·9%).

The identity and purity of this salt were established by hydrolysing 1·675 g. with aqueous sodium hydroxide, and acidifying the solution, when 0·67 g. of *m*-nitrobenzoic acid, m. p. 140°, was precipitated, and 0·16 g., m. p. 130°, collected from the filtrate by means of ether, the total yield being 99%. Both crops were identified as *m*-nitrobenzoic acid by the mixed-melting point method, and the first crop was also analysed (Found : C, 50·5; H, 3·0. Calc., C, 50·3; H, 3·0%).

2-*Phenyl*-4 : 5-*dihydroglyoxaline*.—Hofmann (*Ber.*, 1888, **21**, 2334) states, without giving any details, that this base is best prepared by heating dibenzoylethylenediamine in a stream of hydrogen chloride, and this method was adopted after it had been found that dibenzoylethylenediamine was completely hydrolysed by boiling with concentrated sulphuric acid (3 c.c. per g.) for 10 minutes, and was only slowly attacked by boiling concentrated hydrochloric acid (10 c.c. per g.) when, after 2 hours, 82% was recovered unchanged. Ten grams of dibenzoylethylenediamine (prepared from ethylenediamine monohydrate by the Schotten-Baumann method in 91% yield) were heated to 250°, and dry hydrogen chloride was passed through the molten substance for 1 hour. The product was dissolved in hot water; on keeping, benzoic acid and 0·3 g. of unchanged material separated. The filtrate was basified and extracted with ether, which gave 4·56 g. of 2-phenyl-4 : 5-dihydroglyoxaline, m. p. 100° (yield 83·7%). It crystallised from acetone in colourless, prismatic needles, m. p. 102—103° (corr.). Hofmann gives m. p. 101°.

The nitrate crystallises from acetone in large, colourless, rhombic prisms, which are hydrated to a variable extent. After drying at 98°, it is anhydrous and melts at 118—119° (corr.) after softening from 117°. On cooling, it resolidifies and then melts sharply at 123° (corr.), but on recrystallising this modification, it reverts to the original form, m. p. 118—119°. This salt was described previously by Forssel (*Ber.*, 1892, **25**, 2135), who does not record its m. p.

Nitration of 2-*Phenyl*-4 : 5-*dihydroglyoxaline*.—The anhydrous

nitrate (10·55 g.) was added to concentrated sulphuric acid (21 c.c.) cooled in ice and salt. The solution was kept for 1 hour at room temperature and then heated for 2 hours at 100°. The product was treated with barium hydroxide and barium chloride, just as the nitration product of benzamidine, to give the hydrochloride, which was crystallised from alcohol, when 10·47 g. of pure 2-*m*-nitrophenyl-4 : 5-dihydroglyoxaline hydrochloride were obtained, that is, 84·4%. The mother-liquors contained hydrochlorides (m. p. 195—200°) which could not be separated either as such or as hydriodide or picrate, and the material was therefore oxidised with alkaline permanganate, when a mixture of nitrobenzoic acids was obtained, from which pure *m*-nitrobenzoic acid was isolated in a yield of 3%.

2-m-*Nitrophenyl*-4 : 5-*dihydroglyoxaline hydrochloride* crystallises from alcohol in coarse, yellow needles containing $1H_2O$, which is lost at 100°. After drying, it has m. p. 249—251° (corr.). It is readily soluble in water or hot alcohol, but sparingly soluble in acetone (Found in air-dried salt : loss in a vacuum over H_2SO_4, 7·4, 7·3. $C_9H_9O_2N_3,HCl,H_2O$ requires H_2O, 7·3%. Found in dried salt : C, 47·6; H, 4·3; Cl, 15·6. $C_9H_9O_2N_3,HCl$ requires C, 47·5; H, 4·4; Cl, 15·6%). The *hydriodide* crystallises from water in pale yellow, prismatic needles, m. p. 207—209° (corr.), which are anhydrous and sparingly soluble in water (Found : I, 40·0. $C_9H_9O_2N_3,HI$ requires I, 39·8%).

The *picrate* crystallises from water or alcohol in fine, lemon-yellow needles, m. p. 224—225° (corr.). It is anhydrous and sparingly soluble in hot water or hot alcohol, but very readily soluble in acetone.

The orientation of the nitro-group in 2-*m*-nitrophenyl-4 : 5-dihydroglyoxaline was established by oxidation. The hydrated hydrochloride (1·23 g.) in hot water (50 c.c.) was boiled with 17% aqueous sodium hydroxide (20 c.c.) and sufficient aqueous potassium permanganate to give a permanently pink solution. After adding alcohol and filtering, the solution was concentrated and acidified with hydrochloric acid, when 0·577 g. of *m*-nitrobenzoic acid, m. p. 140° (corr.), was deposited, whilst ether extracted a further 0·048 g., m. p. 125—128°, from the mother-liquor. Mixtures of the two crops with pure *m*-nitrobenzoic acid had m. p. 140° (corr.) and 132—135°, respectively. The total yield is 74·9%.

Bromination of 2-*Phenylglyoxaline*.—A solution of 1·75 c.c. of bromine (1 mol.) in chloroform (15 c.c.) was added gradually to 2-phenylglyoxaline (5 g.) in chloroform (40 c.c.). After keeping for 15 minutes, the colourless precipitate of 4 : 5-dibromo-2-phenylglyoxaline hydrobromide, m. p. 250—255°, was collected, and this

gave on repeated treatment with cold water the base (4·3 g.), m. p. 137—138°. The chloroform mother-liquors were distilled with steam to remove solvent and excess of bromine, and the aqueous residue deposited 0·5 g. of the crude dibromo-base, m. p. 136—138°. The total yield is thus 46%. The final mother-liquors were basified with sodium carbonate and gave crude 2-phenylglyoxaline (2·5 g.; m. p. 138—140°).

4 : 5-*Dibromo*-2-*phenylglyoxaline* crystallises from acetone in colourless cubes, which decompose at about 141° (corr.) after darkening earlier (Found : C, 36·0; H, 2·0; Br, 52·8. $C_9H_6N_2Br_2$ requires C, 35·8; H, 2·0; Br, 53·9%). It is insoluble in cold water and resinifies when heated with water. It is soluble in warm dilute mineral acids, aqueous sodium hydroxide, or ammonia. It is readily soluble in alcohol or acetone, and fairly readily soluble in ether or chloroform.

The *hydrochloride* crystallises from dilute hydrochloric acid in colourless needles, m. p. 235—237° (corr.). It yields the base on treatment with water. The *picrate* forms yellow plates, from alcohol, m. p. 170—172° (corr.).

Nitration. Potassium nitrate (3·3 g.; 1 mol.) was added to a cold solution of 4 : 5-dibromo-2-phenylglyoxaline (10 g.) in concentrated sulphuric acid (40 c.c.). After heating for 2 hours at 100°, the solution was poured into water, when 4 : 5-dibromo-2-*p*-nitrophenylglyoxaline was precipitated; the filtrate was basified with sodium carbonate, when an isomeric base separated. After crystallising these products from alcohol, 7·0 g. of the *p*-nitro-compound (yield 63%) and 0·2 g. of the isomeride (yield 1·8%) were obtained in a pure state.

4 : 5-*Dibromo*-2-p-*nitrophenylglyoxaline* crystallises from alcohol in orange needles, m. p. 220—222° (corr.) (Found in air-dried base : loss in a vacuum over H_2SO_4, 9·3, 9·3. $C_9H_5O_2N_3Br_2,2H_2O$ requires $2H_2O$, 9·4%. Found in dried base : C, 31·2; H, 1·8; N, 12·1; Br, 45·8. $C_9H_5O_2N_3Br_2$ requires C, 31·1; H, 1·4; N, 12·1; Br, 46·1%). It is insoluble in cold water, and resinifies on heating with water. It is insoluble in cold dilute mineral acids, but dissolves slightly on warming. It dissolves in aqueous sodium hydroxide, ammonia, and sodium carbonate, giving red, orange, and yellow solutions, respectively. It is readily soluble in alcohol, acetone, or ether. On oxidation with alkaline permanganate, it gave *p*-nitrobenzoic acid, which was identified by the mixed-melting point method. 4 : 5-*Dibromo*-2-o(or m)-*nitrophenylglyoxaline* crystallises from dilute alcohol in lemon-yellow, glistening plates, m. p. 181—182° (corr.), which are anhydrous (Found : C, 31·0; H, 2·0; N, 12·1. $C_9H_5O_2N_3Br_2$ requires C, 31·1; H, 1·4; N, 12·1%). It is insoluble

in hot or cold water, slightly soluble in dilute mineral acids, and readily soluble in aqueous sodium hydroxide, ammonia, or sodium carbonate, giving red, orange, and yellow solutions. The quantity available did not permit the identification of the acid produced on oxidation.

Reduction of 4 : 5-*Dibromo-2-phenylglyoxaline.*—Hot solutions of 4 : 5-dibromo-2-phenylglyoxaline (5 g.) in alcohol (125 c.c.) and hydrated sodium sulphite (20·5 g.) in water (200 c.c.) were mixed and boiled for 8 hours under reflux. After the alcohol had been removed, a crystalline precipitate (m. p. 185—187°) was deposited, which was separated, by fractional precipitation by hydrochloric acid from its solution in aqueous sodium hydroxide, into 4(5)-bromo-2-phenylglyoxaline (1·43 g.; m. p. 205—206°; yield 39%) and unchanged dibromo-base (1·36 g.).

4(5)-*Bromo-2-phenylglyoxaline* crystallises from dilute alcohol in small, white needles, m. p. 206—207° (corr.) (Found: C, 48·3; H, 3·1; N, 12·2; Br, 35·7. $C_9H_7N_2Br$ requires C, 48·4; H, 3·1; N, 12·6; Br, 35·9%). It is slightly soluble in hot water, readily soluble in alcohol or acetone, and moderately readily soluble in ether. It is soluble in warm dilute acids, aqueous sodium hydroxide, or ammonia, but insoluble in aqueous sodium carbonate.

The *hydrochloride* crystallises from dilute hydrochloric acid in hard, white needles, which lose $1H_2O$ in a vacuum over sulphuric acid and then melt at 118—119° (corr.) (Found in air-dried salt: loss in a vacuum over H_2SO_4, 6·6. $C_9H_7N_2Br,HCl,H_2O$ requires H_2O, 6·5%. Found in dried salt: Cl, 13·8. $C_9H_7N_2Br,HCl$ requires Cl, 13·7%). On heating at 100°, the vacuum-dried salt suffers a further loss owing to dissociation. The *picrate* crystallises from alcohol in yellow plates, m. p. (air-dried) 164—165° (corr.).

Nitration. Potassium nitrate (0·76 g.; 1 mol.) was added to a cold solution of 4(5)-bromo-2-phenylglyoxaline (2 g.) in concentrated sulphuric acid (4 c.c.). After heating for 2 hours at 100°, the solution was poured into water, filtered from a yellow precipitate (1·0 g.; m. p. 95—110°), which was not worked up, and basified with sodium carbonate, when a further precipitate (1·7 g.; m. p. 180—182°) was collected. After crystallisation from dilute alcohol, this gave pure 4(5)-bromo-2-*p*-nitrophenylglyoxaline (0·75 g.; yield 31%).

4(5)-*Bromo*-2-p-*nitrophenylglyoxaline* crystallises from glacial acetic acid in yellow needles, m. p. 222—223° (corr.) (Found: loss at 100°, 18·1. $C_9H_6O_2N_3Br,CH_3{\cdot}CO_2H$ requires loss of $CH_3{\cdot}CO_2H$, 18·3%. Found in substance dried at 100°: C, 40·0; H, 2·5; N, 15·8. $C_9H_6O_2N_3Br$ requires C, 40·3; H, 2·2; N, 15·7%).

It is insoluble in hot water, readily soluble in alcohol, ether, acetone, or glacial acetic acid, and moderately readily soluble in

chloroform. It is soluble in aqueous mineral acids, and dissolves in aqueous alkalis, including sodium carbonate, giving yellow to red solutions.

On oxidation with alkaline permanganate, it gave *p*-nitrobenzoic acid, which was identified by the mixed-melting point method.

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UNIVERSITY OF MANCHESTER. [*Received, January 21st*, 1926.]

CIX.—*Derivatives of Tetrahydrocarbazole. Part V. Carboxylic Acids.*

By WINIFRED MAUDE COLLAR and SYDNEY GLENN PRESTON PLANT.

THE tetrahydrocarbazolecarboxylic acids hitherto described have the carboxyl group either in the reduced portion of the carbazole molecule (Perkin, J., 1904, **85**, 418; Baeyer and Tutein, *Ber.*, 1889, **22**, 2184) or attached to the nitrogen atom (Perkin and Plant, J., 1923, **123**, 683). We have now prepared the four isomeric acids in which the carboxyl group is attached to the benzene nucleus (for the scheme of numbering the positions in tetrahydrocarbazole, see J., 1923, **123**, 677) by Fischer's method for the synthesis of indole derivatives. In this way, the hydrazones made by condensing *cyclo*hexanone with *o*- and *p*-hydrazinobenzoic acid lost ammonia and gave respectively *tetrahydrocarbazole*-8- and 6-*carboxylic acids*, whilst the hydrazone from *m*-hydrazinobenzoic acid by the same process gave a mixture of two acids, one of which must have the carboxyl group in the 5- and the other in the 7-position. This experience is contrary to that which was found in the case of *cyclo*hexanone-*m*-nitrophenylhydrazone, from which only one of the two possible isomeric nitrotetrahydrocarbazoles, assumed to be 7-nitrotetrahydrocarbazole, was obtained on closing the indole ring (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 68; Perkin and Plant, J., 1921, **119**, 1828). Baeyer and Tutein (*loc. cit.*) prepared an acid which may be tetrahydrocarbazole-2 or 4-carboxylic acid from the phenylhydrazone of *cyclo*hexanone-3-carboxylic acid.

The constitutions of these four tetrahydrocarbazolecarboxylic acids are confirmed by the fact that they easily give tetrahydrocarbazole on distillation with soda-lime.

EXPERIMENTAL.

Tetrahydrocarbazole-6-*carboxylic Acid.*—The crude hydrochloride of *p*-hydrazinobenzoic acid, prepared from *p*-aminobenzoic acid (25 g.) by the method of Fischer (*Annalen*, 1882, **212**, 337), was

dissolved in hot water (350 c.c.), treated with an excess of sodium acetate, and then with *cyclo*hexanone (18 c.c.); on shaking, cyclo*hexanone*-p-*carboxyphenylhydrazone* separated. It crystallised from glacial acetic acid in yellow prisms, m. p. 236° (decomp.) (Found : N, 12·5. $C_{13}H_{16}O_2N_2$ requires N, 12·1%).

The crude hydrazone was added to water (200 c.c.) and sulphuric acid (40 c.c.) and the mixture warmed to boiling. The *tetrahydrocarbazole*-6-*carboxylic acid* that separated crystallised from dilute alcohol in colourless plates, m. p. 282° (Found : N, 6·6. $C_{13}H_{13}O_2N$ requires N, 6·5%).

The *methyl* ester was produced by boiling the acid with methyl alcohol containing a little sulphuric acid for 4 hours, and precipitating by the addition of dilute aqueous ammonia. It crystallised from dilute acetic acid in colourless leaves, m. p. 158° (Found : N, 5·9. $C_{14}H_{15}O_2N$ requires N, 6·1%). The *ethyl* ester was prepared in a similar way and separated from dilute alcohol in small, colourless prisms, m. p. 119°.

Tetrahydrocarbazole-8-*carboxylic Acid*.—The hydrochloride of *o*-hydrazinobenzoic acid was converted by a process similar to that described above into cyclo*hexanone*-o-*carboxyphenylhydrazone*, which separated from benzene in pale yellow needles, m. p. 162° (Found : N, 12·0. $C_{13}H_{16}O_2N_2$ requires N, 12·1%). On warming the hydrazone (6 g.) with water (120 c.c.) and sulphuric acid (30 c.c.), *tetrahydrocarbazole*-8-*carboxylic acid* separated and, on recrystallisation from benzene, it was obtained in colourless prisms, m. p. 203° (Found : N, 6·5. $C_{13}H_{13}O_2N$ requires N, 6·5%).

The *methyl* ester crystallises from methyl alcohol in long, colourless prisms, m. p. 124° (Found : N, 5·9. $C_{14}H_{15}O_2N$ requires N, 6·1%). The *ethyl* ester separates from dilute alcohol in colourless needles, m. p. 76° (Found : N, 5·8. $C_{15}H_{17}O_2N$ requires N, 5·7%).

Tetrahydrocarbazole-5- and 7-*carboxylic Acids*.—cyclo*Hexanone*-m-*carboxyphenylhydrazone*, prepared from *m*-hydrazinobenzoic acid in the usual way, crystallised from dilute alcohol in orange prisms, m. p. 176° (decomp.) (Found : N, 11·9. $C_{13}H_{16}O_2N_2$ requires N, 12·1%). The crude hydrazone was converted into a mixture of *tetrahydrocarbazole*-5- and 7-*carboxylic acids* on warming with dilute sulphuric acid. The two acids were isolated from the product by fractional crystallisation from either glacial acetic acid or aqueous acetone, and purified by conversion into their methyl esters, from which they were readily obtained on saponification. The acid which separated first in both cases was finally recrystallised from glacial acetic acid and obtained in colourless prisms, m. p. 287° (Found : N, 6·6. $C_{13}H_{13}O_2N$ requires N, 6·5%). Its *methyl* ester crystallised from methyl alcohol in colourless needles, m. p.

155°, and its *ethyl* ester from dilute alcohol in small, colourless plates, m. p. 146°.

The isomeric *tetrahydrocarbazolecarboxylic acid* was ultimately obtained from glacial acetic acid in almost colourless prisms, m. p. 210° (Found: N, 6·1. $C_{13}H_{13}O_2N$ requires N, 6·5%). Its *methyl* ester separated from aqueous alcohol in colourless prisms, m. p. 93° (Found: N, 6·1. $C_{14}H_{15}O_2N$ requires N, 6·1%).

The higher-melting acid (m. p. 287°) is the main constituent of the product of this reaction and from 30 g. of the crude material 16 g. of this acid and 6 g. of the isomeride (m. p. 210°) were isolated in a pure condition.

THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, January 20th*, 1926.]

CX.—*The Oximes of* 2:4-*Dinitrobenzil and the Beckmann Change.*

By GERALD BISHOP and OSCAR L. BRADY.

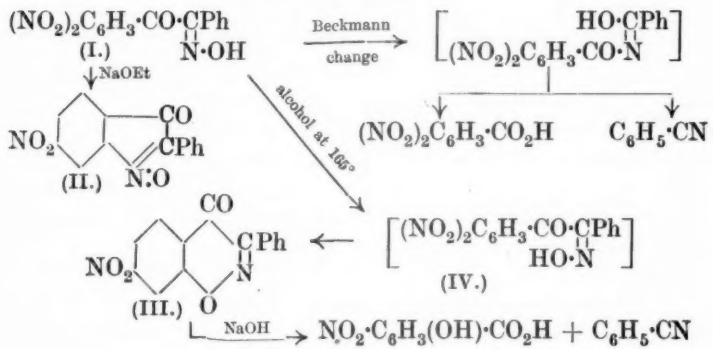
IN a previous communication (J., 1922, **121**, 2364), two substances, regarded as monoximes of 2:4-dinitrobenzil, were described to which, on account of their behaviour in the Beckmann change, the following structures were assigned:

$$\underset{\alpha.}{(NO_2)_2C_6H_3\cdot CO\cdot \overset{\overset{|}{N}}{\underset{HO}{C}}Ph} \qquad \underset{\beta.}{(NO_2)_2C_6H_3\cdot \overset{\overset{|}{N}}{\underset{HO}{C}}\cdot COPh}$$

Further investigation, however, has shown that the supposed β-oxime was a mixture and that its reactions were untrustworthy guides to its constitution. Consequently, our early view of the configurations of the substances requires modification. We are now of opinion that their reactions are best explained by adopting Meisenheimer's view that the Beckmann change takes place in a *trans-* and not in a *cis*-sense (*Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289), ring closure being assumed to involve no change in configuration (compare, however, Kuhn and Ebel, *Ber.*, 1925, **58**, 919; Böeseken, *ibid.*, p. 1470; Meisenheimer, *ibid.*, p. 1491). The α-oxime has accordingly been given the configuration (I). The Beckmann change leads to benzonitrile and 2:4-dinitrobenzoic acid as previously described. By boiling with the calculated quantity of sodium dissolved in alcohol, the α-oxime is converted, by elimination of nitrous acid, into a brilliant scarlet compound which, on account of its colour, we consider to be 6-*nitro*-3-*keto*-

2-phenyl-ψ-indole-1-oxide (II), the α-oxime, since the oxygen atom is remote from the nitro-group, reacting in the nitrone form. This compound on treatment with excess of alkali gives benzaldehyde and an amorphous compound, thus behaving similarly to the α-oxime itself when treated with excess of aqueous sodium hydroxide. When the α-oxime is heated in alcohol to 165°, nitrous acid is eliminated and *7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine* (III) is formed. That this compound is not produced by the action of alkali on the α-oxime suggests that at the high temperature the oxime undergoes an isomeric change analogous to that of the oximes of benzil under similar conditions; in the new oxime (IV) thus produced, the hydroxyl and nitro-groups are vicinal and consequently nitrous acid is readily eliminated. 7-Nitro-4-keto-3-phenyl-1 : 2-benzoxazine on hydrolysis gives benzonitrile and 4-nitrosalicylic acid. The benzoxazine melts, by an unfortunate coincidence, at the same temperature (169°) as 4-nitrosalicylonitrile, and we have found that the compound produced by the action of alkali on the supposed β-oxime and described in our previous paper as 4-nitrosalicylonitrile (*loc. cit.*, p. 2369), and for the identification of which we relied on the melting point and hydrolysis to 4-nitrosalicylic acid, was in fact this benzoxazine.

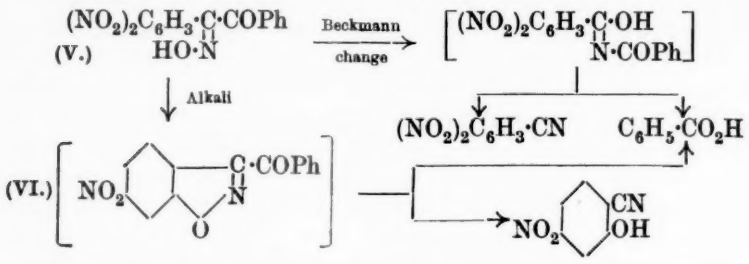
The reactions of the α-oxime may be summarised thus :



The action of excess of free hydroxylamine on 2 : 4-dinitrobenzil, by which the supposed β-oxime was obtained, yields a complex mixture, from which 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine (III), the α-oxime (I), and the pure β-oxime (V) have been isolated. The formation of the benzoxazine suggests that the unknown oxime (IV) is first produced and loses nitrous acid with great ease in the presence of excess of hydroxylamine.

The β-oxime, in the Beckmann change, gives benzoic acid and 2 : 4-dinitrobenzonitrile. On heating with alkali, it gives benzoic

acid and 4-nitrosalicylonitrile through the unstable *iso*oxazole (VI). Its reactions may be represented thus:



There was also evidence that the crude oximation mixture contained the fourth oxime, $(NO_2)_2C_6H_3\cdot C(N\cdot OH)\cdot COPh$. The presence of this would account for the isolation, in the previously described experiments, of 2 : 4-dinitroaniline after the supposed β-oxime had undergone the Beckmann change. In a subsequent similar experiment with the crude oximation mixture, we were unable to separate the dinitroaniline from the other products, but isolated 2 : 4-dinitrophenol by heating with concentrated alkali, acidifying, and distilling in steam.

EXPERIMENTAL.

α-2 : 4-*Dinitrobenzilmonoxime*.—The preparation is described in our previous paper. The α-monoxime (3 g.) was heated for 5 hours with absolute alcohol (5 c.c.) in a sealed tube at 165°. On cooling, a colourless, crystalline compound separated which after crystallisation from alcohol gave 7-*nitro*-4-*keto*-3-*phenyl*-1 : 2-*benzoxazine* (III), m. p. 169° (Found : N, 10·4. $C_{14}H_8O_4N_2$ requires N, 10·4%). This compound was identical in properties with the supposed 4-nitrosalicylonitrile previously obtained by the action of alkali on the impure β-oxime (Bishop and Brady, *loc. cit.*) and on admixture did not depress its melting point. 7-Nitro-4-keto-3-phenyl-1 : 2-benzoxazine was boiled for a short time with 10% sodium hydroxide; the odour of benzonitrile was observed and on distilling in steam this nitrile was obtained in the distillate; the residue, on being acidified, gave a precipitate from which 4-nitrosalicylic acid was obtained by crystallisation.

The action of alkali in excess on the α-oxime was described in the previous paper. When, however, the oxime (5 g.), dissolved in absolute alcohol (20 c.c.) containing the calculated quantity of sodium to give the sodium salt (0·36 g.), was boiled for 15 minutes, a brilliant scarlet precipitate of 6-*nitro*-3-*keto*-2-*phenyl*-ψ-*indole* 1-*oxide* formed which crystallised from alcohol as a red, crystalline

powder, m. p. 198° (Found : C, 62·5; H, 3·1; N, 10·5. $C_{14}H_8O_4N_2$ requires C, 62·7; H, 3·0; N, 10·4%). Nitrite was detected in the mother-liquor from the preparation. Boiled with excess of aqueous alkali, the compound behaves in a similar manner to the α-oxime, giving benzaldehyde and an amorphous product.

β-2 : 4-*Dinitrobenzilmonoxime.*—A solution of 2 : 4-dinitrobenzil in alcohol cooled in ice was treated with an alcoholic solution of 3 equivalents of hydroxylamine. After a few moments, crystals of 7-nitro-4-keto-3-phenyl-1 : 2-benzoxazine began to separate and after 12 hours these were collected and the filtrate from them was diluted with water (¼ vol.); a small quantity of impure α-monoxime was then precipitated. The filtrate from the α-oxime was poured into excess of water, kept over-night, and the precipitate repeatedly crystallised from dilute alcohol until its melting point was constant; β-2 : 4-dinitrobenzilmonoxime, m. p. 168°, was thus obtained (Found : N, 13·4. Calc., N, 13·3%).

A solution of the β-oxime in ether was cooled in ice, and the calculated quantity of phosphorus pentachloride added. After 12 hours, ice-water was added, and the mixture then kept for 3 hours. The ether layer was shaken several times with 2*N*-sodium carbonate and evaporated; 2 : 4-dinitrobenzonitrile, identified by comparison with an authentic specimen, was thus obtained. The alkaline extracts on acidification and re-extraction with ether gave benzoic acid.

The β-oxime was boiled under reflux for an hour with 2*N*-sodium hydroxide; no darkening or evolution of ammonia occurred as with the α-oxime, and on cooling and saturating with carbon dioxide 4-nitrosalicylonitrile crystallised. This was identified by comparison with a specimen prepared from 2 : 4-dinitrobenzaldoxime (Borsche and Oppenheimer, *Annalen*, 1912, **390**, 10). The carbonate solution, after removal of dissolved nitrosalicylonitrile with ether, gave benzoic acid on being acidified and extracted with ether.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, January 25th*, 1926.]

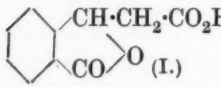
CXI.—*Synthetical Work on the* iso*Quinoline Alkaloids. Part II. A Method of Opening the Rings of Cyclic Ketones.*

By GEORGE ALFRED EDWARDS.

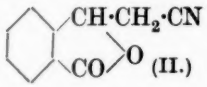
THE reactions herein described were investigated with the object of obtaining derivatives of β-*o*-cyanophenylpropionic acid and of *o*-carboxyphenylacetonitrile, such substances being required for attempts to synthesise ten-membered rings of the cryptopine type.

The sodium salt of 1-nitroso-β-naphthol when heated to 180° with sand gives sodium *o*-cyanocinnamate in poor yield (D.R.-P. 116223). This reaction was examined in the hope of bringing about the same change by less violent means. 1-Nitroso-β-naphthol was converted by benzoyl chloride and cold caustic soda solution into a benzoyl derivative, which slowly hydrolysed in warm caustic soda solution, yielding benzoic acid and the *o*-cyanocinnamic acid of m. p. 137° (D.R.-P. 411955). The separation of the benzoic acid was rather troublesome, so it is fortunate that benzoyl chloride can be replaced by either benzene- or toluene-sulphonyl chloride, the acyl derivative produced being in each case easily hydrolysed to the above cyano-acid.

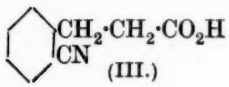
This 2-cyanocinnamic acid was at first thought to be o-*carboxycinnamonitrile*, since on hydrolysis it gave *o*-carboxycinnamic acid, and since, if its formation followed the normal course of the Beckmann reaction, ring opening might take place in two ways, thus: $R{\cdot}C(:NOH){\cdot}COR' \longrightarrow R{\cdot}CO{\cdot}NH{\cdot}COR' \longrightarrow$ either $R{\cdot}CO_2H$ and $R'CN$ or RCN and $R'{\cdot}CO_2H$. *o*-Carboxycinnamonitrile was therefore synthesised as follows. Phthalylacetic acid (Neumann and Gabriel, *Ber.*, 1893, **26**, 952) was reduced electrolytically to phthalideacetic acid (I). This was converted through its acid chloride into *phthalideacetamide*, which, when boiled in xylene solution with phosphorus pentoxide, lost water and gave *phthalideacetonitrile* (II). The



(I.)



(II.)



(III.)

lactone ring of this substance was opened on treatment with caustic soda, and by carefully heating the sodium salt in a vacuum *o*-carboxycinnamonitrile was produced.

If the acyl derivatives of 1-nitroso-β-naphthol are heated at 140° for a short time, they will give the *o*-cyanocinnamic acid of m. p. 255—256° on hydrolysis.

The low-melting acid itself, when heated above its melting point for a few minutes, is completely converted into the high-melting *o*-cyanocinnamic acid. Since both cyano-acids on electrolytic reduction give β-o-*cyanophenylpropionic acid* (III), the only possible conclusion is that these acids are geometric isomerides similar to cinnamic and *allo*cinnamic acids. On the analogy of these, the low-melting acid has been called *o*-cyano*allo*cinnamic acid.

As β-*o*-cyanophenylpropionic acid was required in quantity, the most suitable conditions for its preparation were investigated. A method is described, using toluenesulphonyl chloride, which is suitable for large-scale preparations; about 6% of the acyl derivative

is hydrolysed to 1-nitroso-β-naphthol, but this is easily separated owing to its insolubility in sodium carbonate solution.

Since in these reactions 1-nitroso-β-naphthol obviously reacted in the oxime form, it seemed probable that substances containing the group $\cdot CH_2 \cdot CO \cdot$ in a ring, if first converted into their *iso*nitroso-derivatives, would react with acid chlorides in the same way. This was investigated in the case of the hydrindones. Hydrindone itself gave *o*-carboxyphenylacetonitrile in 92% yield, whilst 5 : 6-dimethoxy- and 5 : 6-methylenedioxy-hydrindones gave the corresponding cyano-acids. These three cyano-acids have recently been prepared by Haworth and Pink (J., 1925, **127**, 1369) by the action of phosphorus pentachloride on the nitrosohydrindones. They easily decompose on warming, but by cautious treatment with thionyl chloride may be converted into their acid chlorides, from which their esters, amides, and substituted amides may be obtained.

Experimental.

Action of Benzenesulphonyl Chloride upon 1-*Nitroso*-β-*naphthol.*—1-Nitroso-β-naphthol (1 g.-mol.) is mixed with benzenesulphonyl chloride (1 g.-mol.), the whole is dissolved in the minimum quantity of cold acetone, and 8% caustic soda solution (1·2 g.-mols.) is added slowly, with shaking and cooling in ice. The *benzenesulphonyl-1-nitroso*-β-*naphthol* that separates crystallises from a little acetone in yellow prisms, m. p. 124—125° (decomp.) (Found: C, 61·6; H, 3·6. $C_{16}H_{11}O_4NS$ requires C, 61·3; H, 3·5%). On being kept at its m. p. for a few minutes, it resolidifies and thereafter melts at 137—139°, having been converted into an isomeride which crystallises from acetone in cream needles, m. p. 141° (Found: C, 61·7; H, 3·5%).

The low-melting acyl derivative is hydrolysed when dissolved in a slight excess of 8% caustic soda solution at 60°. The filtered cooled solution on acidification deposits *o*-cyano*allo*cinnamic acid in almost colourless needles. This crystallises from water, containing a little animal charcoal, in colourless, felted needles, m. p. 137° (Found: C, 69·7; H, 4·4. Calc. for $C_{10}H_7O_2N$: C, 69·4; H, 4·1%). When the benzenesulphonyl derivative, m. p. 141°, is treated in the same way, *o*-cyanocinnamic acid separates in a gelatinous form; it crystallises from glacial acetic acid in slightly brown, glistening plates, m. p. 256°, identical with the product of heating the sodium salt of 1-nitroso-β-naphthol with sand at 180°.

Direct Preparation of o-*Cyano*allo*cinnamic Acid.*—A solution of 1-nitroso-β-naphthol (43 g.) and toluenesulphonyl chloride (47 g.) in the minimum quantity of acetone is kept at 55—60° while caustic soda (8% solution) is added slowly, with constant shaking, so that

the solution is kept faintly alkaline. When the solution finally becomes permanently alkaline, it is cooled, filtered, and acidified, 38 g. of crude *o*-cyano*allo*cinnamic acid being precipitated. For the preparation of *o*-cyanophenylpropionic acid further purification is unnecessary.

o-Carboxycinnamic acid, m. p. 182°, is produced when either of the *o*-cyanocinnamic acids is refluxed for 2 hours with 10% caustic soda solution, and is precipitated on acidification.

β-*o*-*Cyanophenylpropionic Acid* (III).—A solution of crude *o*-cyano*allo*cinnamic acid (40 g.) in 14% sodium carbonate solution (150 c.c.) is filtered from insoluble gummy impurities and reduced electrolytically for 3 hours at a lead cathode, the current density being 2 amps./100 sq. cm.; the anode cell consists of a lead electrode in 20% caustic soda solution. The product on acidification deposits a slightly brown, sandy powder, which crystallises from water in prisms, m. p. 127° (Found: C, 68·9; H, 5·0. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·2%).

o-*Carboxycinnamonitrile*, $CO_2H{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CN$.—Phthalylacetic acid (40 g.) dissolved in caustic soda (200 c.c. of 15% solution) is reduced electrolytically under the conditions described above. The hot solution is acidified with hydrochloric acid and filtered; on cooling, phthalideacetic acid separates in colourless plates, m. p. 151°, identical with the substance obtained by the reduction of phthalylacetic acid with sodium amalgam (Gabriel and Michael, *Ber.*, 1877, **10**, 391). The acid (10 g.) is boiled with thionyl chloride (20 c.c.) for 15 minutes, the excess of thionyl chloride distilled away, the gummy residue dissolved in a little chloroform, and the solution slowly added to aqueous ammonia (60 c.c.; *d* 0·880) cooled in ice, the temperature being kept below 10° during the addition. The chloroform is then evaporated on the water-bath; on cooling, *phthalideacetamide* separates in rectangular plates, m. p. 182—183° (Found: N, 7·5. $C_{10}H_9O_3N$ requires N, 7·3%). This amide (2 g.) is heated in boiling xylene (16 c.c.) with phosphorus pentoxide (4 g.) for 15 minutes. The boiling filtered xylene, on cooling, deposits pure white needles, m. p. 111°, of *phthalideacetonitrile*, and more may be obtained by extracting the brown, gummy residue from the xylene with boiling water, the latter depositing slightly brown needles on cooling. The nitrile is insoluble in cold alkali, but dissolves readily on warming, ammonia being evolved from the boiling solution.

A solution of phthalideacetonitrile in the theoretical quantity of warm caustic soda solution is evaporated to dryness on the water-bath, the residue kept at 200° in a vacuum for 10 minutes, cooled, and dissolved in water. On acidification a slightly yellow powder

separates which crystallises from water as a microcrystalline powder, m. p. 169—172° (Found: N, 7·3. $C_{10}H_9O_3N$ requires N, 7·3%). This is o-*carboxycinnamonitrile* and yields *o*-carboxycinnamic acid, m. p. 182°, on hydrolysis (as above).

o-*Carboxyphenylacetonitrile.*—2-*iso*Nitroso-1-hydrindone (7·2 g.) is dissolved in caustic soda (80 c.c. of 8% solution), and benzenesulphonyl chloride (9 g.) added with constant shaking. The benzenesulphonyl derivative first separates as a white gum, which slowly dissolves on raising the temperature to 80° for a few minutes. The cooled filtered solution on acidification deposits *o*-carboxyphenylacetonitrile as a white powder crystallising from water in colourless needles, m. p. 126°, identical with the substance obtained by Haworth and Pink (*loc. cit.*).

2-*Carboxy*-4 : 5-*dimethoxyphenylacetonitrile* is obtained from dimethoxy*iso*nitrosohydrindone (3 g.), caustic soda (3 g. in 25 c.c. of water), and benzenesulphonyl chloride (2·2 c.c.) by the method described above; it crystallises slowly in needles, m. p. 166—167°.

2-*Carboxy*-4 : 5-*methylenedioxyphenylacetonitrile*, obtained in exactly the same way as the dimethoxy-compound, crystallises in slightly yellow prisms, m. p. 195° (Found: C, 58·3; H, 3·4. Calc., C, 58·5; H, 3·4%).

The author wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which covered the cost of the materials used in this investigation.

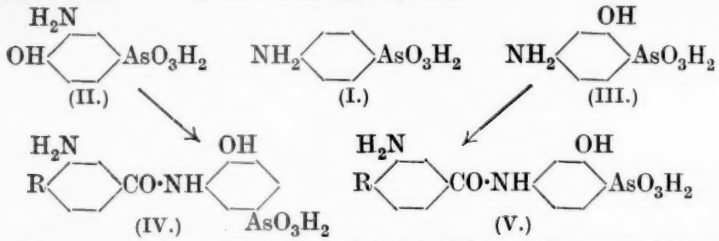
KING'S COLLEGE, LONDON. [*Received, January 4th*, 1926.]

CXII.—*Trypanocidal Action and Chemical Constitution. Part IV. Arylamides of Aminohydroxyphenylarsinic Acids.*

By LESLIE FRANK HEWITT and HAROLD KING.

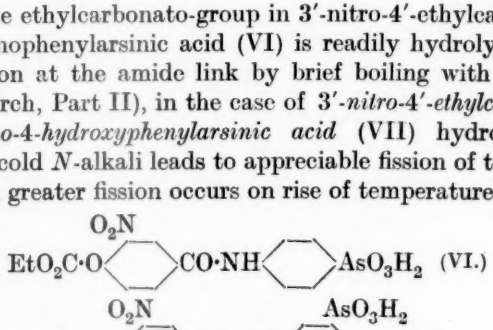
IN Parts I and II (King and Murch, J., 1924, **125**, 2595; 1925, **127**, 2632) the preparation and properties of a number of arylamides of 4-aminophenylarsinic acid (I) were described. Inasmuch as Fourneau and his colleagues (*Ann. Inst. Pasteur*, 1923, **37**, 551) have shown that on *Trypanosoma brucei* in mice, 3-amino-4-hydroxyphenylarsinic acid (II) and 4-amino-2-hydroxyphenylarsinic acid (III) with chemo-therapeutic indices (curative dose/tolerated dose) of 1/5 and 1/8 respectively are superior to 4-aminophenylarsinic acid with an index of 1/1, it was thought of interest to introduce into these hydroxy-acids certain substituted aminobenzoyl radicals

which were shown in Part II to have a favourable influence on the trypanocidal activity of 4-aminophenylarsinic acid.



The types (IV) and (V), where R is H, OMe, or OH, were obtained by reduction of the corresponding nitro-acids by ferrous chloride and alkali, the preparation of the nitrohydroxybenzoyl derivatives (R = OH) necessitating the use of ethylcarbonatonitrobenzoyl chloride, where the hydroxyl group is protected by the carbethoxyl group.

Although the ethylcarbonato-group in 3′-nitro-4′-ethylcarbonatobenzoyl-4-aminophenylarsinic acid (VI) is readily hydrolysed with negligible fission at the amide link by brief boiling with *N*-alkali (King and Murch, Part II), in the case of 3′-*nitro*-4′-*ethylcarbonatobenzoyl*-3-*amino*-4-*hydroxyphenylarsinic acid* (VII) hydrolysis of this group by cold *N*-alkali leads to appreciable fission of the amide link and much greater fission occurs on rise of temperature.



The maximum dose tolerated by mice, expressed in milligrams per gram of mouse, and the minimum curative dose, where determined, on an experimental infection of *T. equiperdum* in mice, of this group of twelve related compounds is shown below, *R* signifying the para-substituent to the amide group and *r* the number of days before relapse occurred.

Type IV. Derivatives of 3-$NH_2$4-OHC_6H_3·AsO_3H_2.

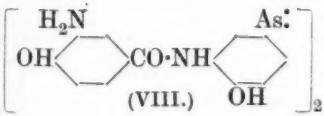
	Nitro-acids.			Amino-acids.		
R	H.	OMe.	OH.	H.	OMe.	OH.
Dosis tolerata	0·075	0·2	0·4	0·3	0·2	0·3
Dosis curativa ...	—	—	—	0·3 (r = 13)	0·15 (r = 4)	0·3 (r = 8)

Type V. Derivatives of 4-$NH_2$2-OHC_6H_3·AsO_3H_2.

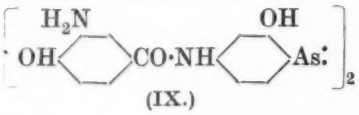
Dosis tolerata	0·2	0·2	0·3	0·1	0·6	0·2
Dosis curativa ...	—	—	—	0·1 (r = 12)	0·3 (r > 30)	0·2 (r = 12)

On comparing these results with those obtained for the corresponding derivatives of 4-aminophenylarsinic acid (Part II) it will be observed that there is here no enhanced trypanocidal activity such as might be expected from the relative activities of the parent mono-nuclear arsinic acids (I, II, and III). There is, however, a rough parallelism between the activities of the amides of 4-aminophenylarsinic acid and those of 4-amino-2-hydroxyphenylarsinic acid; in each case, the aminoanisoyl derivative is the only one of the three amides with permanent curative properties.* Expressed otherwise, one might say that the introduction of the 2-hydroxyl group into derivatives of 4-aminophenylarsinic acid has not radically altered the distribution of the main and residual affinities of the molecule on which trypanocidal activity as measured by the two determinants, curative dose and tolerated dose, ultimately depends.

The possession by the six complex amino-arsinic acids above described of a free hydroxyl group emphasised the desirability of the preparation of the corresponding arseno-derivatives, which like salvarsan should be administrable by solution in alkali. The comparison of six arseno-bases with the parent amino-acids was all the more a desideratum because Fourneau has expressed the opinion that on the evidence available the arsinic acids are at least as active as the arseno-derivatives. Unfortunately this object was only realisable in part because, unexpectedly, the possession of a single hydroxyl group in the same nucleus as the arseno-group did not confer alkaline solubility, the sodium salts of the aminobenzoyl and aminoanisoyl derivatives being quite insoluble in water. In addition, the hydroxyl group ortho to the arseno-group in derivatives of 4-amino-2-hydroxyphenylarsinic acid weakens the attachment of the arsenic atom to the nucleus, thus leading under very mild conditions of reduction by hypophosphorous acid to formation of products containing polyarsenides. This is perhaps not surprising, because the parent acid, 4-amino-2-hydroxyphenylarsinic acid, when reduced by the same reagent gives no arseno-base but only free arsenic. The hydroxyaminobenzoyl derivatives (VIII) and (IX) were, however, alkali-soluble, the former substance being of



(VIII.)



(IX.)

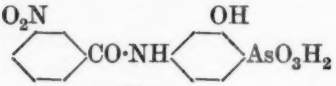
* In this series of communications, the term "permanent curative property" indicates no relapse of some of the animals within 30 days, the blood being examined almost daily over that period. As a rule, each dose is tried on five mice.

special interest because of the duplication of the *o*-aminophenol grouping contained in salvarsan. The maximum tolerated and the minimum curative dose of these two arseno-bases in comparison with their parent arsinic acids are shown below.

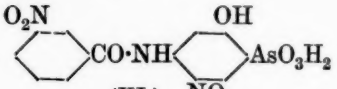
	Acid.	Arseno (VIII).	Acid.	Arseno (IX).
Dosis tolerata	0·3	0·075	0·2	0·075
Dosis curativa	0·3	0·03	0·2	0·02
	($r = 8$)	($r = 5$)	($r = 12$)	($r > 30$)

Whilst there is little difference in activity between the arseno-derivative (VIII) and its parent acid, the arseno-derivative (IX) is permanently curative on one-fourth of its tolerated dose and is thus far superior to its parent acid. It should, however, be borne in mind that the arseno-derivative (IX) contains a certain proportion of polyarsenides, as has been indicated above.

3′-Nitrobenzoyl-4-amino-2-hydroxyphenylarsinic acid (X) on further nitration yields exclusively *3′ : 5-dinitrobenzoyl-4-amino-2-hydroxyphenylarsinic acid* (XI), which on reduction yields the corresponding *diaminobenzoylaminohydroxyphenylarsinic acid.*



(X.)



(XI.)

In Part II it was shown that the diamino-arsinic acids were in general permanently curative, but this substance, either on its maximum tolerated dose or on lower doses, was completely devoid of action. Various reasons might be advanced for this, but it is not proposed to discuss them here.

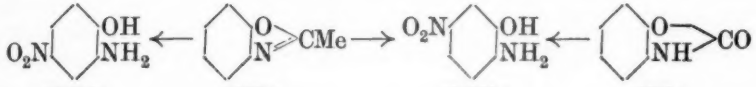
On hydrolysis of (XI) by alkali *5-nitro-4-amino-2-hydroxyphenylarsinic acid* was obtained and this on reduction gave a new *4 : 5-diamino-2-hydroxyphenylarsinic acid* of which only one isomeride is known. The activity of this diamino-acid in comparison with the closely related 4-amino-2-hydroxyphenylarsinic acid (III) and 3-amino-4-hydroxyphenylarsinic acid (II) is shown in the following table:

	Diamino-acid.	III.	II.
Dosis tolerata	0·3	0·5	1·5
Dosis curativa	0·05 ($r = 16$)	0·2	0·3

The diamino-acid was very erratic in its curative action and far inferior to (II) or (III). It will be noticed that the indices for (II) and (III) are not as favourable on *T. equiperdum* as those obtained by Fourneau (see opening paragraph) on *T. brucei*.

4-Amino-2-hydroxyphenylarsinic acid (III), required in quantity in this investigation, was prepared by the Bart-Schmidt reaction from 5-nitro-2-aminophenol (Bauer, *Ber.*, 1915, **48**, 1582). The

preparation of the latter from 2-aminophenol presents some points of interest to the student of orientation. Meldola and Wechsler (P., 1900, 180) showed that *ON*-diacetyl-2-aminophenol on attempted mononitration gave exclusively 4 : 6-dinitro-2-aminophenol (picramic acid) after hydrolysis, and we find in support that both mono- and tri-acetyl-2-aminophenol on mononitration yield after hydrolysis almost exclusively picramic acid, although in the case of triacetyl-2-aminophenol traces of both 5-*nitro*- and 4-*nitro*-2-*acetylaminophenol* have been isolated. In D.R.-P. 165650, however, 5-nitro-2-aminophenol is said to be prepared by the nitration of ethenyl-2-aminophenol (XII). An examination of this reaction shows that 5-nitro-2-aminophenol (XIII) is indeed formed together with 4-nitro-2-aminophenol (XIV) in the ratio 4 : 1, the main bulk of the 5-nitro-compound after hydrolysis being separable owing to its lesser solubility in water. The remaining mixture can be separated by fractionally crystallising the acetates from benzene, which obviates both the tendency of the two isomerides to separate from water as brilliant red mixed crystals and the formation of the low-melting hydrate of the 4-nitro-derivative.



(XIV.) (XII.) (XIII.) (XV.)

The sulphonation product of carbonyl-2-aminophenol (XV) is known to yield 2-aminophenol-5-sulphonic acid on hydrolysis (D.R.-P. 197496; King, J., 1921, **119**, 1117), but although 5-nitrocarbonyl-2-aminophenol is prepared by the action of nitric acid on carbonylaminophenol and yields nitrocatechol on alkaline hydrolysis (Chelmicki, *J. pr. Chem.*, 1890, **42**, 441), there is no record of its hydrolysis by acids. This should also lead to the required 5-nitro-2-aminophenol. This has now been effected, but only with difficulty, as 5-nitrocarbonyl-2-aminophenol is very resistant to acid hydrolysis. Of the two possible routes to the required nitroaminophenol, the one *via* the ethenyl derivative proved the more convenient.

Thus, whilst the nitration of any of the acetyl derivatives of 2-aminophenol yields as main product picramic acid in which the orienting power of the hydroxyl may be said to overwhelm that of the acetylated amino-group in agreement with the behaviour of 4-aminophenol derivatives, in ethenyl- and carbonyl-aminophenol the reverse is true. The latter cases are also in agreement with the nitration of another cyclic derivative of 2-aminophenol, acetylphenoxazine, which yields 3 : 9-dinitrophenoxazine, the nitro-

groups entering the para-position to the nitrogen atom (Kehrmann and Saager, *Ber.*, 1903, **36**, 477).

To Miss F. M. Durham and Miss J. Marchal of this department we again tender our thanks for the efficient and painstaking care bestowed on the biological side of our subject.

Experimental.

o-*Aminophenol.*—The large quantities of *o*-aminophenol required were prepared in part by an improvement on Grandmougin's process (*Ber.*, 1906, **39**, 3561). *o*-Nitrophenol dissolved in 2*N*-sodium hydroxide (1 mol.) was treated with solid sodium hyposulphite (1·6 mols.) and sufficient sodium hydroxide to keep the reaction mixture faintly alkaline, the solution being well stirred and the temperature kept below 30°. The yield of *o*-aminophenol, including ether-extracted material, was 67%.

*Nitration of Ethenyl-*o*-aminophenol* (XII).—Ethenyl-*o*-aminophenol was obtained in 90% yield by a simplification of Ladenburg's method (*Ber.*, 1876, **9**, 1524). *o*-Aminophenol (carefully freed from inorganic salts) was distilled with 3 parts of acetic anhydride, and the distillate refractionated through a short column. The fraction, b. p. 200—210°, consisted of ethenyl-*o*-aminophenol. Of this, 53·9 g. were dissolved in sulphuric acid (200 c.c.) below 0° and treated with nitric acid (*d* 1·42; 1·1 mols.) dissolved in an equal volume of sulphuric acid. On pouring on to ice, a bulky yellow compound was obtained, but attempts to isolate a pure nitroethenyl-*o*-aminophenol from this were unsuccessful. (When dried in a vacuum, it lost 90% of its weight and liquefied, and repeated crystallisation from alcohol gave eventually pure 5-*nitro*-2-*acetylaminophenol*.) The wet, bulky precipitate was heated at 100° with 325 c.c. of hydrochloric acid (*d* 1·16) until dissolved, and the solution almost neutralised. Orange needles of 5-nitro-2-aminophenol (37·7 g.) separated immediately. On adjusting the reaction of the filtrate to neutrality, a red, crystalline solid (9·4 g.) separated which was almost pure 4-nitro-2-aminophenol. On one crystallisation from benzene with addition of glacial acetic acid, it yielded the pure *acetate*, yellow sheaves, which on drying at 95° gave 8·5 g. of the pure base. Ether extraction of the mother-liquors gave a semi-solid product which, fractionally crystallised as acetate from benzene and a little glacial acetic acid, gave further small quantities of 5-nitro-2-aminophenol (1·8 g.) and 4-nitro-2-aminophenol (3·0 g.). The total yield of pure nitroaminophenols was 83%.

5-Nitro-2-aminophenol (XIII) when quite pure melts at 203—204° and crystallises from water in orange or dark brown needles (Friedlaender and Zeitlin, *Ber.*, 1894, **27**, 192, give m. p. 201—202°).

This compound was also obtained as green plates, which melted at 170°, but crystallised almost instantaneously, and then melted at 203—204°. The velocity of transformation in contact with aqueous solutions is, however, slow. The N-*monoacetyl* derivative, obtained by the action of acetic anhydride without the application of heat, is sparingly soluble in boiling alcohol and crystallises in stout, pale yellow prisms, m. p. 271—272° (Found : C, 49·0; H, 4·1. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·1%). The ON-*diacetyl* derivative is formed very readily by boiling the aminonitrophenol with acetic anhydride. It is readily soluble in boiling alcohol and crystallises as a felt of fine needles, m. p. 193—194° (Found : C, 50·5; H, 4·3. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2%). The *triacetyl* derivative was isolated from the acetylation mother-liquors of the preceding. It crystallises from absolute alcohol, in which it is readily soluble, in fern-like clusters of stout crystals, m. p. 138—139° (Found : C, 51·6; H, 4·5. $C_{12}H_{12}O_6N_2$ requires C, 51·4; H, 4·3%).

4-Nitro-2-aminophenol (XIV) forms an N-*monoacetyl* derivative, m. p. 279—280°, by the action of acetic anhydride at room temperature. It forms clusters of needles from absolute alcohol, in which it is very sparingly soluble at the boiling point (Found : C, 48·9; H, 4·2. $C_8H_8O_4N_2$ requires C, 49·0; H, 4·1%). The ON-*diacetyl* derivative, formed with difficulty by long boiling with excess of acetic anhydride, crystallises from boiling absolute alcohol, in which it is readily soluble, in needles or prisms, m. p. 187—188° (Found : C, 50·2; H, 4·3. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2%).

Nitration of Carbonyl-o-aminophenol (XV).—Carbonyl-*o*-aminophenol (0·5 g.) was warmed with 2 c.c. of nitric acid (*d* 1·42); a violent reaction then occurred accompanied by frothing. The mononitro-compound crystallised out and was isolated by pouring into water. The yield was 0·5 g., m .p. 255° (Bender, *Ber.*, 1886, **19**, 2271, gives m. p. 256°). When boiled for 6 hours with 16% hydrochloric acid, it was for the most part undissolved and unchanged, but neutralisation of the filtrate and ether extraction gave 0·15 g. of 5-nitro-2-aminophenol, m. p. 201°. The unchanged residue was boiled with hydrochloric acid (32%) and alcohol for 8 hours and gave a portion of unchanged compound and 0·2 g. of 5-nitro-2-aminophenol.

Nitration of N-*Acetyl-2-aminophenol.*—On nitration with nitric acid (1 mol.) as described for ethenyl-2-aminophenol, the sole product obtained was 4 : 6-dinitro-2-acetylaminophenol (acetylpicramic acid).

Nitration of Triacetyl-2-aminophenol.—When nitrated with nitric acid (1 mol.) as for the ethenyl derivative, this phenol yields small quantities of the monoacetyl derivatives of 4- and 5-nitro-2-amino-

phenol, readily isolated by reason of their sparing solubility in alcohol. If, however, the nitration product be hydrolysed, 4 : 6-dinitro-2-aminophenol (picramic acid) is readily isolated as the main product of the nitration.

4-Amino-2-hydroxyphenylarsinic Acid (III).—4-Nitro-2-hydroxyphenylarsinic acid was obtained in 78% yield from 5-nitro-2-aminophenol as described by Bauer (*loc. cit.*) except that the main bulk of arsinic acid separated on neutralisation to Congo-paper, without proceeding *via* the magnesium salt. On reduction with ferrous chloride by the method of Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1580) it gives an 84% yield of 4-amino-2-hydroxyphenylarsinic acid. The *hydrochloride*, *nitrate*, and *sulphate* all crystallise from the corresponding *N*-acids in acicular crystals, and with the exception of the sulphate are readily soluble on warming. On addition of nitrite, a yellow colour is developed, and on adding to alkaline β-naphthol, a red colour is produced. The same colour is produced by pouring into alkali, probably through self-coupling. Addition of excess of nitrite destroys the coupling property almost instantaneously.

3′-Nitrobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (X).—The *m*-nitrobenzoylation was carried out exactly as described for the isomeric 3-amino-4-hydroxyphenylarsinic acid, an 89% yield of the amide being obtained. It is almost insoluble in hot glacial acetic acid, but slightly soluble in hot 90% formic acid, from which it crystallises in bunches of needles (Found : As, 19·5. $C_{13}H_{11}O_7N_2As$ requires As, 19·6%). The *sodium* salt crystallises in fine needles.

3′-Aminobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (V; R = H).—This acid was prepared as described for the isomeric derivative of 3-amino-4-hydroxyphenylarsinic acid (*vide infra*) in 72% yield. Liberated from acid solution by sodium acetate, it separates microcrystalline (Found : As, 20·8; 20·7. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). The *sodium* salt crystallises in platelets, the *ammonium* salt as a felt of needles. The *hydrochloride*, clusters of needles, and *nitrate*, minute needles, are readily soluble in their respective warm *N*-acids, but the *sulphate*, clusters of needles, is rather sparingly soluble in boiling *N*-sulphuric acid.

The *arseno*-derivative prepared by the action of hypophosphorous acid at 60° contained 30% of As as against 24·8% (theoretical) and consisted therefore mainly of polyarsenides. It was insoluble in sodium hydroxide or mineral acids, but dissolved on adding nitrite.

3′ : 5-Dinitrobenzoyl-4-amino-2-hydroxyphenylarsinic Acid (XI).—The above-described mononitro-acid (11·3 g.) was dissolved in sulphuric acid (45 c.c.), cooled to 0°, and nitrated with a mixture

of 2·15 c.c. of nitric acid (*d* 1·42) and sulphuric acid (2 c.c.). On pouring on to ice, a yellow, microcrystalline precipitate separated. It was collected, dissolved in sodium carbonate, and reprecipitated by acid. The yield was 95% (Found: As, 17·7. $C_{13}H_{10}O_9N_3As$ requires As, 17·6%). This acid is sparingly soluble in boiling acetic acid and crystallises in microscopic needles, more soluble in formic acid, from which it separates in much longer needles.

On hydrolysis by boiling with 15 volumes of *N*-sodium hydroxide for 40 minutes, it gave pure *m*-nitrobenzoic acid, and *5-nitro-4-amino-2-hydroxyphenylarsinic acid*, short, yellow prisms crystallising readily from hot water, in which it is fairly readily soluble. It is sparingly soluble in 3*N*-hydrochloric acid, but readily soluble in concentrated acid. It diazotises with nitrite and thereafter couples with alkaline β-naphthol. Excess of nitrite, however, destroys the coupling property (Found: As, 27·1. $C_6H_7O_6N_2As$ requires As 27·0%).

3′ : 5-Diaminobenzoyl-4-amino-2-hydroxyphenylarsinic Acid.—This was obtained in 71% yield by reduction of the dinitro-acid with ferrous chloride and alkali. When liberated from the alkaline extracts of the ferric hydroxide, it separates in very fine needles, but occasionally as an amorphous, voluminous solid which becomes crystalline on warming the precipitation liquor (Found: As, 20·6. $C_{13}H_{14}O_5N_3As$ requires As, 20·4%). The *hydrochloride* is very soluble in *N*-hydrochloric acid, but separates from stronger acid in narrow leaflets with domed ends; the *sulphate*, minute needles, is only moderately soluble in *N*-sulphuric acid, but the *nitrate* is very readily soluble in *N*-nitric acid and crystallises from more concentrated acid in needles and in lenticular prisms. On addition of nitrite, it diazotises and then gives the same red colour on pouring into alkali, probably owing to self-coupling, as on adding to alkaline β-naphthol. This acid is very resistant to hydrolysis. It is unchanged after boiling with *N*-alkali for an hour, or after 7 hours' boiling with concentrated hydrochloric acid. It was recovered to the extent of more than 60% after 5 hours' heating with concentrated hydrochloric acid under pressure at 150°. *m*-Aminobenzoic acid was identified as a hydrolytic product.

4 : 5-Diamino-2-hydroxyphenylarsinic Acid.—5-Nitro-4-amino-2-hydroxyphenylarsinic acid (2·0 g.) was dissolved in 22 c.c. of *N*-sodium hydroxide (3 mols.) at 0° and to the vigorously stirred solution were added all at once 5·0 g. of sodium hyposulphite (1 mol. of 80% = 4·7 g.) with removal of the external bath. After being stirred for 2 hours, the solution was filled with fine needles of the required amino-acid. This was collected and washed with ice-cold water (yield 93%). For analysis and physiological testing, it was

dissolved in 20 c.c. of 0·7*N*-hydrochloric acid and reprecipitated by addition of saturated sodium acetate. On 1·65 g. there was a loss of 0·1 g. The *diamino-acid* crystallises from boiling water, in which it is sparingly soluble, in fine needles. It is very soluble in *N*-hydrochloric acid and gives, on addition of nitrite, a red coloration, which becomes pale after a few seconds. This is followed by separation of the *diazoimine*, in rectangular leaflets. The diamino-acid reduces ammoniacal silver nitrate instantly at room temperature. In acid solution, potassium dichromate gives a port wine colour (Found: As, 29·0. $C_6H_9O_4N_2As,\frac{1}{2}H_2O$ requires As, 29·0%).

3′-Nitroanisoyl-4-amino-2-hydroxyphenylarsinic Acid.—Prepared in 83% yield in the same way as its isomeride (*vide infra*), this acid is almost insoluble in hot glacial acetic acid, but crystallises from hot 90% formic acid in spear-shaped needles (Found: As, 18·4. $C_{14}H_{13}O_8N_2As$ requires As, 18·2%). The *sodium* salt, silky needles, and *ammonium* salt, diamond-shaped plates, were only moderately soluble in water.

3′-Aminoanisoyl-4-amino-2-hydroxyphenylarsinic Acid (V; R = OMe).—This acid, obtained in 77% yield by reduction of the nitro-acid with ferrous chloride and alkali at 0°, separates as a jelly on acidification of the alkaline extracts of the ferric hydroxide. It soon crystallises, however, in silky needles (Found: As, 19·4. $C_{14}H_{15}O_6N_2As$ requires As, 19·6%). The *sodium* salt crystallises in prisms readily soluble in water. The *hydrochloride*, spiked leaflets, is readily soluble in warm *N*-hydrochloric acid, but the *sulphate*, short, white needles and stout prisms, and *nitrate*, soft, woolly needles, are much less soluble in the warm *N*-acids.

The *arseno*-base could not be obtained sufficiently pure for physiological testing. Reduction with hypophosphorous acid under the mildest conditions gave polyarsenides containing between 26% and 56% of arsenic as against 22·6% required by theory. Reduction with hyposulphite even at 70° gave no trace of arseno-base.

3′-Nitro-4′-ethylcarbonatobenzoyl-4-amino-2-hydroxyphenylarsinic Acid.—3-Nitro-4-ethylcarbonatobenzoyl chloride (28·2 g.; 2 mols.) was added in several portions to 4-amino-2-hydroxyphenylarsinic acid (12 g.), dissolved in 2*N*-sodium hydroxide (45 c.c.), saturated sodium acetate solution (50 c.c.), and water (20 c.c.), with vigorous shaking. The reaction mixture was acidified to Congo-paper, and the precipitate collected after being well washed with dilute acid and water. When dry, it was extracted in a Soxhlet apparatus with ether and reprecipitated from sodium carbonate solution by acid. The yield was 73% of the theoretical. This acid is practically insoluble in hot glacial acetic acid, but separates from 90% formic

acid in microscopic, fluffy needles (Found : As, 15·9. $C_{16}H_{15}O_{10}N_2As$ requires As, 15·9%).

3′-Nitro-4′-hydroxybenzoyl-4-amino-2-hydroxyphenylarsinic Acid.—The preceding acid (18·5 g.) was dissolved in 4 equivalents of *N*-sodium hydroxide (158 c.c.) and kept at room temperature for 18 hours. On acidification carbon dioxide and ethyl alcohol were liberated and a white, microcrystalline precipitate was thrown down. This was collected, dried, and extracted with ether in a Soxhlet apparatus (yield 89%). This acid dissolves in alkali with a bright yellow colour, is almost insoluble in warm acetic acid, but crystallises from 90% formic acid in microscopic needles (Found : As, 18·8. $C_{13}H_{11}O_8N_2As$ requires As, 18·8%).

3′-Amino-4′-hydroxybenzoyl-4-amino-2-hydroxyphenylarsinic Acid (V; R = OH).—Reduced as described for its isomeride (*vide infra*), this acid was obtained in 76% yield. Liberated from alkaline solutions by acid, it separates in a gelatinous condition, but rapidly crystallises, on warming, in elongated leaflets (Found : As, 20·0. $C_{13}H_{13}O_6N_2As$ requires As, 20·4%). The *hydrochloride*, small needles, is readily soluble in *N*-hydrochloric acid; the *nitrate*, diamond-shaped plates, is sparingly soluble in hot *N*-nitric acid, and the *sulphate*, needles, is moderately soluble in warm *N*-sulphuric acid. On adding nitrite to a salt with mineral acids, a very sparingly soluble yellow *diazo-oxide* is precipitated, of amorphous appearance, but microscopically anisotropic. It couples intensely with alkaline β-naphthol.

3′-Amino-4′-hydroxybenzoyl-4-amino-2-hydroxyarsenobenzene (IX).—The above-described arsinic acid (3 g.) was suspended in 15 c.c. of hypophosphorous acid (*d* 1·14), diluted with an equal volume of water, and stirred at 45° for 2½ hours after addition of a crystal of potassium iodide. The orange-yellow arsenohypophosphite was worked up as described for aminobenzoyl-3-amino-4-hydroxyarsenobenzene. The yield was 1·0 g. When dried, it formed a brittle, brownish-yellow powder, instantly soluble in sodium hydroxide to a pale yellow solution. It was not soluble in mineral acids, but dissolved on adding nitrite and then coupled with alkaline β-naphthol. On analysis, the product proved to contain polyarsenide (Found : As, 28·7. $C_{26}H_{22}O_6N_4As_2$ requires As, 23·6%). When prepared at 55°, the proportion of polyarsenide was increased, as the arsenic content was 29·8%.

3′-Nitrobenzoyl-3-amino-4-hydroxyphenylarsinic Acid.—To a solution of 3-amino-4-hydroxyphenylarsinic acid (7·4 g.) in 2*N*-sodium hydroxide (25 c.c.) and half-saturated sodium acetate solution (200 c.c.) was added 3-nitrobenzoyl chloride (11·8 g.) dissolved in ether. The mixture was vigorously shaken, and sodium

hydroxide solution run in from time to time to maintain a slight alkalinity to phenolphthalein. On completion of the reaction, the mixture was made neutral to Congo-paper, the precipitated solid collected, washed with dilute acid, and, after drying, extracted thoroughly with ether. It was dissolved in alkali, reprecipitated by acid, dried, and again extracted with ether. The yield was 90%. This nitro-acid is almost insoluble in hot glacial acetic acid, but crystallises from hot 90% formic acid in silky needles (Found: As, 19·6. $C_{13}H_{11}O_7N_2As$ requires As, 19·6%). The *ammonium* salt is sparingly soluble and crystallises in tufts of needles.

3′-*Aminobenzoyl*-3-*amino*-4-*hydroxyphenylarsinic Acid* (IV; R = H).—The nitro-acid (7·6 g.) was dissolved in 72 c.c. of 2*N*-sodium hydroxide solution at 0°, and ferrous chloride (28 g.) dissolved in 40 c.c. of water run in slowly with vigorous stirring. A further quantity (72 c.c.) of 2*N*-sodium hydroxide was then run in under the same conditions. After stirring for 90 minutes, the ferric hydroxide was filtered off and extracted twice by thorough disintegration with 150 c.c., each time, of 0·5*N*-sodium hydroxide. The combined alkaline filtrates were neutralised to Congo-paper, and the crystalline precipitate was collected. It was dissolved in 150 c.c. of *N*-hydrochloric acid and reprecipitated by addition of saturated sodium acetate solution. The yield was 44%. This amino-arsinic acid, so prepared, separates in microscopic platelets of indefinite shape (Found: loss at 100°, 4·9, 4·7, 5·1. $C_{13}H_{13}O_5N_2As,H_2O$ requires H_2O, 4·9%. Found in anhydrous material: As, 20·8. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%). It is readily soluble in warm *N*-mineral acids, the *hydrochloride* crystallising in microscopic, narrow leaflets, the *sulphate* in rectangular leaflets, and the *nitrate* in microscopic plates.

3′-*Aminobenzoyl*-3-*amino*-4-*hydroxyarsenobenzene*.—The corresponding arsinic acid (1 g.) was suspended in a mixture of 30% hypophosphorous acid (5 c.c.), glacial acetic acid (5 c.c.), and water (5 c.c.), with addition of a crystal of potassium iodide. After stirring for 2 hours at 57°, the orange-yellow solid was centrifuged off, and the deposit washed several times with boiled-out water. It was then made alkaline by addition of aqueous sodium hydrogen carbonate and washed free from alkali by repeated centrifuging with water. The product was dried in a vacuum (yield 0·53 g.). This arsenobenzene is insoluble in aqueous acids or alkalis, but soluble in warm 90% formic acid. In acid solution, it dissolves immediately on addition of nitrite and then couples with alkaline β-naphthol with a deep red colour (Found: As, 24·8. $C_{26}H_{22}O_4N_4As_2$ requires As, 24·8%).

3′-*Nitroanisoyl*-3-*amino*-4-*hydroxyphenylarsinic Acid*.—This acid

was obtained in 80% yield by the same process as is described for the corresponding 3′-nitrobenzoyl derivative. It is practically insoluble in boiling glacial acetic acid, but crystallises from 90% formic acid in square leaflets (Found: As, 17·9. $C_{14}H_{13}O_8N_2As$ requires As, 18·2%). The *sodium* salt, acicular crystals, is readily soluble in water.

3′-*Aminoanisoyl*-3-*amino*-4-*hydroxyphenylarsinic Acid* (IV; R = OMe).—The reduction of the nitro-compound was carried out precisely as described for the preparation of the 3′-aminobenzoyl compound. The yield was 61%. Liberated from acid solution by sodium acetate, this acid crystallises in colourless plates (Found: As, 20·0. $C_{14}H_{15}O_6N_2As$ requires As, 19·6%). The *hydrochloride*, rosettes of needles, is readily soluble in hot *N*-hydrochloric acid, the *sulphate*, microscopic, square leaflets, is less soluble in hot *N*-sulphuric acid, and the *nitrate*, long, silky needles, is sparingly soluble in hot *N*-nitric acid.

3′-*Aminoanisoyl*-3-*amino*-4-*hydroxyarsenobenzene*.—Prepared in the same way as the previously described arsenobenzene in 77% yield, this is a yellow powder insoluble in acids or alkalis, but instantly soluble in acid solution on addition of nitrite. It then couples with alkaline β-naphthol (Found: As, 22·7. $C_{28}H_{26}O_6N_4As_2$ requires As, 22·6%).

3′-*Nitro*-4′-*ethylcarbonatobenzoyl*-3-*amino*-4-*hydroxyphenylarsinic Acid* (VII).—3-Amino-4-hydroxyphenylarsinic acid (11·6 g.) was dissolved in 100 c.c. of water with addition of 5·3 g. (2 mols.) of sodium carbonate. After addition of 100 c.c. of saturated sodium acetate solution, 27·3 g. (2 mols.) of 3-nitro-4-ethylcarbonatobenzoyl chloride were added in three portions with a few c.c. of ether, and well shaken. After ½ hour, the solution was made definitely acid to Congo-paper, and the mixture of acids collected, dried, and divided by ether extraction into 17·0 g. of the required arsinic acid, insoluble in ether, and 16·0 g. of recovered nitroethylcarbonatobenzoic acid, soluble in ether. This arsinic acid is readily soluble in cold 90% formic acid and crystallises therefrom in microscopic needles; from glacial acetic acid, in which it is readily soluble when hot, it separates either as needles or rectangular leaflets (Found: As, 16·1. $C_{16}H_{15}O_{10}N_2As$ requires As, 15·9%).

3′-*Nitro*-4′-*hydroxybenzoyl*-3-*amino*-4-*hydroxyphenylarsinic Acid*.—The foregoing ethylcarbonato-acid (10 g.) was dissolved in *N*-sodium hydroxide (4 mols.) and kept for a day. It was diluted with an equal volume of water and precipitated with concentrated hydrochloric acid. On warming the mixture, the precipitated acid became partly crystalline. The dried acid, when extracted with ether to remove hydroxynitrobenzoic acid, was obtained in 84% yield. The

aqueous mother-liquors, extracted with ether, gave nitrohydroxybenzoic acid and also contained 3-amino-4-hydroxyphenylarsinic acid, as was proved by its coupling strongly with alkaline β-naphthol after diazotisation. The required arsinic acid dissolves in alkali with a bright yellow colour. It crystallises in diamond-shaped spicules from either boiling glacial acetic acid, in which it is sparingly soluble, or boiling 90% formic acid, in which it is readily soluble (Found: As, 19·2. $C_{13}H_{12}O_8N_2As$ requires As, 18·8%).

3′-Amino-4′-hydroxybenzoyl-3-amino-4-hydroxyphenylarsinic Acid. (IV; R = OH).—The nitro-acid (8·8 g.) was dissolved in 33 c.c. of water with the aid of two equivalents (23 c.c.) of 2*N*-sodium hydroxide, and ferrous chloride (31 g.) in 42 c.c. of water added slowly with vigorous stirring at −5°. Sufficient sodium hydroxide (167 c.c. of 2*N*) was now slowly added to make the reaction of the fluid distinctly alkaline to litmus. The filtered ferric hydroxide was thoroughly extracted, each time, with 170 c.c. of 0·2*N*-sodium hydroxide. On rendering the combined extracts neutral to Congo-paper, a copious separation of crystalline amino-acid ensued. This was purified by solution in 100 c.c. of *N*-nitric acid at 50° and precipitation with sodium acetate, and gave 4·0 g. The main mother-liquors were rapidly concentrated below 50° to a small volume and gave a mixture of the amino-compound and the corresponding azoxy-compound, readily separable by dilute nitric acid into 0·75 g. of azoxy-compound (9% yield) and 1·0 g. of amino-compound. The total yield of amino-compound was 62% (Found: As, 20·4. $C_{13}H_{13}O_6N_2As$ requires As, 20·4%). The amino-acid diazotises with production of a deep yellow solution, from which an insoluble *diazo-oxide* crystallises in dense clusters of needles. It couples readily with alkaline β-naphthol. The *hydrochloride*, microscopic needles, is very sparingly soluble in boiling *N*-hydrochloric acid; the *sulphate*, leaflets, is sparingly soluble in warm *N*-sulphuric acid; and the *nitrate*, microscopic needles, is readily soluble in warm *N*-nitric acid.

The *azoxy*-compound crystallises very readily from boiling 90% formic acid, in which it is readily soluble, in pale brown, truncate, diamond-shaped plates. It dissolves in ammonia with a pale yellow colour and gives an insoluble magnesium salt on addition of magnesium chloride.

3′-Amino-4′-hydroxybenzoyl-3-amino-4-hydroxyarsenobenzene (VIII was obtained in quantitative yield, allowing for recovered acid, by reduction of the corresponding acid (4·0 g.) with 20 c.c. of hypophosphorous acid (*d* 1·14), 20 c.c. of water, 10 c.c. of acetic acid, and a crystal of potassium iodide at 50—55° for 3 hours. The pure arseno-base was isolated as described for the preceding members.

It is a yellow powder soluble in caustic alkalis, but forming insoluble orange salts with acids. It is instantly soluble to a yellow solution on addition of nitrous acid. From more concentrated solutions, the amorphous *diazo-oxide* separates; this couples with alkaline β-naphthol (Found : As, 23·8. $C_{26}H_{22}O_6N_4As_2$ requires As, 23·6%).

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CXIII.—*Liquid-line Corrosion.*

By ERNEST SYDNEY HEDGES.

THERE are many instances of enhanced corrosion occurring at the liquid line, when a solid is partly immersed in a liquid which has a chemical action on it, or which simply dissolves it. The phenomenon was first described by Spring (*Z. physikal. Chem.*, 1889, **4**, 658) for calcite dissolving in hydrochloric acid and for sucrose and sodium carbonate dissolving in water. He concluded that the extra dissolution was due to an enhanced reactivity of the solvent at the surface. This explanation was denied by Klobukow (*ibid.*, 1890, **5**, 180), who suggested that the greater portion of the solid was protected by the downward streaming of the product, whilst fresh solvent was always being drawn in at the liquid surface. Ganguly and Banerji (*Z. anorg. Chem.*, 1922, **124**, 140) believe that the phenomenon is related to the surface tension of the liquid, since the effect was diminished in the cases they investigated by covering with a layer of oil.

The water-line corrosion of metals offers a special case of great practical importance. Here it is generally held that atmospheric oxygen assists in the corrosion near the surface of the liquid. Evans (compare "Corrosion of Metals," Arnold, 1924, p. 106) takes a more definite point of view and ascribes the effect to the automatic removal of ions from the metal in the vicinity of the water line, through the relatively cathodic nature of the portion above. Watson and Watts (*Trans. Amer. Electrochem. Soc.*, 1923, **44**, 1) investigated many cases of slow corrosion of metals in aqueous solution and concluded that the effect was due to protection of the rest of the metal through the downward flow of the reaction products.

EXPERIMENTAL.

During the course of several years' work on the dissolution of metals in various reagents the author has been continually confronted with this phenomenon, and has had opportunities of studying

it, where the reaction velocity is fairly rapid. These seem to be more suitable and trustworthy conditions than the slow corrosion over periods of several weeks previously investigated.

Strips of zinc and magnesium were partially immersed in *N*-hydrochloric acid. The strips were eaten through along a line about 0·5 mm. above the water line some considerable time before the rest of the metal dissolved. Owing to the vigorous evolution of hydrogen, the reaction products were washed in an upward direction instead of downward, and the effect cannot be due in this case to protection of the metal thereby. Watson and Watts (*loc. cit.*) state that water-line corrosion does not take place when zinc dissolves in hydrochloric acid with disengagement of hydrogen. This statement, however, must be due to error of observation.

The effect has also been repeatedly obtained in the dissolution of magnesium in ammonium chloride solution, dilute sulphuric acid and dilute nitric acid, with zinc in dilute sulphuric acid and dilute nitric acid, and with aluminium in solutions of caustic soda and hydrochloric acid. Scarcely any effect was observed in the dissolution of iron in hydrochloric acid.

In all these cases the rate of gassing was sufficient to prevent any downward streaming of the reaction products. It seemed possible, however, that the depolarising action of oxygen contained in the surface of the solution could account for the increased velocity of corrosion. The experiments were therefore repeated in an atmosphere of hydrogen. Identical results were obtained, and thus it is established that the water-line corrosion of metals occurs in absence of the two causes which have been discussed.

Further evidence against the necessity for oxygen is furnished by the strong preferential liquid-line corrosion when strips of copper or iron are partly immersed in strong solutions of nitric acid. Here, the solution itself is a much more active depolariser than atmospheric oxygen. Again, although iron was not observed to undergo appreciable extra corrosion at the water line in hydrochloric acid, the effect is very marked when a mixture of hydrochloric and nitric acids is used. An idea of the magnitude of the effect is gained from an experiment in which copper sheet 0·022 inch in thickness dissolved in a mixture of 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, and 65 c.c. of water. When the water line was completely cut through, the thickness of the undissolved metal was 0·010 inch.

The excessive corrosion takes place just above the water line, at the place where a film of liquid creeps up the metal, and it seems that the increased velocity of reaction is a property of this film. Further evidence supporting this suggestion is gained from some observations on the dissolution of magnesium and zinc in dilute

acids. At suitable rates of reaction the ascending bubbles of hydrogen coalesce near the end of their course, forming a large bubble on either side of the metal sheet just under the water line. The bubble bursts in a short time, but is immediately formed again. Thus, during the greater part of the reaction, there exists just below the water line a thin film of solution in contact with the metal and bounded by the large bubble of hydrogen. Subsequent examination of the metal showed in every case a roughly circular patch indicative of strong preferential corrosion in the region adjacent to the bubble.

This explanation appears to account for the observation by McCulloch (*J. Amer. Chem. Soc.*, 1925, **47**, 1940) that when a rubber band is wrapped tightly round a piece of iron which is then immersed in dilute hydrochloric acid, the iron is strongly corroded under the rubber band.

The author has also repeated Spring's experiment, dissolving sticks of marble in 0·5*N*-hydrochloric acid and in *N*-nitric acid. Under these conditions, the upward wash of carbon dioxide bubbles causes a visible upward streaming of the soluble product, which can be observed to fall subsequently down the sides of the vessel. Excessive corrosion at the water line occurred in both cases. Here the oxygen theory or the electrolytic theory cannot enter. Gurwitsch also (*Z. physikal. Chem.*, 1924, **109**, 375) has performed experiments where the product of solution is specifically lighter than the solvent and yet found increased activity at the surface of the solution.

In experiments where little or no gas evolution occurred and the reaction products were allowed to flow down the metal, the effect was quite different when the metal broke off at the water line. The piece of metal was found to be progressively thinned from the bottom to the water line, resembling a fine wedge. In the other cases, where downward streaming was prevented, the fallen metal was of uniform thickness as though it had been sawn.

Whilst it may be admitted that the downward streaming of reaction products and depolarisation by oxygen may assist in preferential corrosion at the liquid line in suitable circumstances, these experiments indicate that the phenomenon takes place in absence of these causes, thus supporting the original hypothesis of Spring.

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CXIV.—*Observations on Liquid Boundaries and Diffusion Potentials.*

By Sydney Raymond Carter and Frederick Measham Lea.

During an investigation (J., 1925, **127**, 487, 499) on the *E.M.F.* of systems involving potassium chloride and concentrated acid solutions, it was necessary to set up chains of connecting solutions having potentials which would be readily reproducible and be subject to the minimum fluctuation with time.

Various types of liquid junctions were studied, therefore, and the main results are collected in this paper. Thus in making up the oxidation cell (Pt)|Oxid. salts, x*N*-HCl|(*a*) . . . (*b*) *N*-KCl,Hg_2Cl_2|Hg or (Pt)|Oxid. salts, x*N*-HCl|(*a*) . . . (*b*) *N*-H_2SO_4,Hg_2SO_4|Hg the chain x*N*-HCl|(*a*) . . . (*b*)|*N*-KCl or x*N*-HCl|(*a*) . . . (*b*)|*N*-H_2SO_4 may be completed by connecting the points (*a*) and (*b*) in one of the following ways, (i) directly, (ii) through *N*-hydrochloric acid, (iii) through saturated potassium chloride solution.

A. *Acid–Acid Boundaries of the Type* x*N*-HCl|*N*-HCl.—This type of boundary occurred in scheme (ii), and two modes of formation of this boundary will be described.

(1) The connecting tube from (*a*) carries a tap and dips into hydrochloric acid of the same concentration (x*N*-HCl). Connexion is made to a vessel containing *N*-hydrochloric acid by means of an inverted **U** tube filled with *N*-hydrochloric acid and, as in other cases, plugged at the ends with filter-paper. It makes but little difference, however (about 0·001 volt), if this connecting tube be filled with the x*N*-hydrochloric acid. Diffusion potentials at boundaries so set up show little fluctuation with time.

(2) If the open end of the tube with tap from (*a*) is immersed directly in *N*-hydrochloric acid, complete mixing of the two acid solutions takes place as far as the tap and it is here that the actual liquid junction occurs. If the x*N*-hydrochloric acid be 5*N*, this method gives diffusion potentials differing by about 0·006 volt from those obtained by method A (1).

In the work on the cupric–cuprous potentials, as well as that on the diffusion potentials, method A (1) was invariably employed.

B. *Acid–Salt Boundaries of the Type* HCl|KCl.—(1) Direct connexion between x*N*-hydrochloric acid and *N*-potassium chloride is equivalent to scheme (i) and leads to considerable fluctuations of *E.M.F.* when the value of x is high.

(2) An intermediate solution of *N*-hydrochloric acid between the

two solutions in (1) gives the combination xN-HCl|N-HCl|N-KCl, which is scheme (ii).

The xN-HCl|N-HCl boundary has already been described, and the N-HCl|N-KCl boundary is made as follows. The connecting tube is filled with N-potassium chloride, in which case the diffusion potential is constant to about 0·0010 to 0·0015 volt on standing. If the connecting tube be filled with N-hydrochloric acid, a divergence of about 0·002 volt from the above is observed. Our practice has been to use the potassium chloride solution.

Methods B (1) and (2) give values which differ considerably for the total diffusion potential between xN-hydrochloric acid and N-potassium chloride. For very strong hydrochloric acid solutions ($10N$—$11N$) this difference may amount to as much as 0·020 volt.

C. *Saturated Potassium Chloride Solutions.*—The interposition of a saturated potassium chloride solution between xN-hydrochloric acid and N-potassium chloride reduces the diffusion potential, but does not eliminate it completely for strong hydrochloric acid solutions. For concentrations of hydrochloric acid up to N, the conclusion of various workers is that saturated potassium chloride has no diffusion potential against the hydrochloric acid; but this does not hold for stronger hydrochloric acid solutions. Thus between $9N$-hydrochloric acid and N-potassium chloride the interposition of a saturated potassium chloride solution reduces the diffusion potential from approximately 0·090 volt to 0·050 volt. A direct connexion xN-HCl|N-KCl always gives a lower diffusion potential than that obtained when an intermediate N-hydrochloric acid is introduced; for $9N$-hydrochloric acid it is about 0·015 volt lower.

For $9N$-hydrochloric acid the approximate values of the following diffusion potentials are: xN-HCl|N-KCl, 0·090 volt; xN-HCl|N-HCl|N-KCl, 0·105 volt; xN-HCl|Sat. KCl|N-KCl, 0·050 volt.

D. *Liquid Junctions with Sulphuric Acid of the Type* xN-HCl|N-H_2SO_4.—Very little difference is observed if direct connexion be made between the xN-hydrochloric acid and N-sulphuric acid or N-hydrochloric acid be interposed, giving the xN-HCl|N-HCl|N-H_2SO_4 combination.

Variation of Diffusion Potentials.—For corresponding concentrations, an acid|salt boundary shows more variation with time than an acid|acid boundary. The latter, even for N-hydrochloric acid against $10N$-hydrochloric acid, shows little variation, in general not more than 0·001 volt and usually less. If, however, the xN-hydrochloric acid contains a high concentration of some salt in solution, then the xN-HCl|N-HCl boundary may show a fluctuation of several millivolts.

In making potential measurements, the most consistent results were obtained when fresh boundaries were used wherever possible, and this is the experience of other workers.

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CXV.—*The Hydrolytic Action of Low-pressure Superheated Steam on Salts of the Alkaline-earth Metals.*

By PERCY LUCOCK ROBINSON, HAROLD CECIL SMITH, and HENRY VINCENT AIRD BRISCOE.

ALTHOUGH it is generally realised that many salts are attacked by steam at high temperatures, and it is well known, as an extreme case, that salts like magnesium chloride are largely hydrolysed at temperatures little above the boiling point of water, there is little definite information in the literature as to the general incidence and extent of the hydrolytic action of steam. The recognition that many chlorides and bromides could thus be decomposed, even by the relatively low concentration of steam formed during their dehydration, led to the general use of the well-known Harvard bottling apparatus in atomic weight determinations, but it is in relation to technical processes of thermal decomposition that most references to such phenomena are found, and the following notes indicate their general nature.

The thermal decomposition of witherite is facilitated by the presence of steam (Priestley, *Phil. Trans.*, 1788, **78**, 852; Lenoir, *Jahresber.*, 1867, **13**, 256; Heinz, *Chem. News*, 1902, **85**, 206) and a similar result is observed, apparently, when mixtures of barium carbonate with calcium carbonate and carbon (Jacquelain, *Compt. rend.*, 1851, **32**, 877), and with sodium carbonate (*Dingler's Jour.*, 1884, **254**, 436), are employed.

A patented process describes the hydrolytic decomposition of barium sulphide by steam (Leroy and Segay, D.R.-P. 100969, 1897). Fremy stated that fluorspar is decomposed by steam at a red heat, yielding calcium oxide and hydrogen fluoride (*Ann. Chim. Phys.*, 1856, **47**, 17), but Poulenc later found that strontium fluoride is not decomposed by steam at a red heat (*ibid.*, 1894, **2**, 5). It has been reported (Kunheim, "Über Einwirkung des

Wasserdampfes auf Chlormetalle bei hoher Temperatur," Gottingen, 1861) that when calcined in steam calcium chloride is decomposed less readily than magnesium chloride, but more readily than barium chloride, that this hydrolysis of calcium chloride is incomplete (Pelouze, *Compt. rend.*, 1861, **32**, 1267), and that it is accelerated when silica, alumina, or china clay are present (Solvay, *Dingler's Jour.*, 1885, **255**, 307).

When steam is passed over a red hot mixture of calcium sulphate and sodium chloride, sodium sulphate, lime and hydrogen chloride are produced (Tilghmann, *Dingler's Jour.*, 1847, **106**, 196).

Siemens (*ibid.*, 1863, **169**, 207) reported that if water vapour is passed over a molten mixture of sodium chloride with twice its weight of calcium sulphate, hydrochloric acid, sulphur dioxide, and hydrogen sulphide are evolved, while a mixture of steam and carbon dioxide under the same conditions yields only sulphur dioxide and hydrochloric acid; the residue contained undecomposed sodium chloride, sodium hydroxide, calcium sulphide, calcium oxide, and small traces of sodium thiosulphate and sodium sulphide. It has been pointed out (Buff, *ibid.*, 1864, **172**, 282; Knapp, *ibid.*, 1872, **202**, 513) that in such reactions the materials of the containing vessel, *e.g.*, iron and silica, may play an important part, and the obvious incompatibility of some of the foregoing statements may well be due to such causes.

A recent investigation (Thompson and Tilling, *J. Soc. Chem. Ind.*, 1924, **43**, 39T) has shown that the ferrous sulphide formed, together with free sulphur, on heating pyrites in an inert atmosphere is decomposed (to form ferric oxide and hydrogen sulphide) at a lower temperature in steam than in carbon dioxide or air.

Thus it is evident that the previous investigations of the hydrolytic action of steam are few in number, and with the exception of the last cited, purely qualitative in kind. It has been the object of the present investigation to secure some numerical data in a few typical cases. A weighed quantity of the salt under investigation was heated to a known temperature for a definite time in a current of steam, and the issuing steam was condensed. Titration of this condensate with standard alkali gave a measure of the extent of hydrolytic decomposition which had occurred.

Experimental.

Steam was passed at a constant rate over a weighed quantity of material in a porcelain boat placed in a silica tube heated electrically to the desired temperature. In the hot zone, the silica was protected by a liner-tube of stout sheet nickel. Temperatures were measured by means of a platinum–platinum-rhodium thermo-

couple and a Paul millivoltmeter, the hot junction of the couple being held immediately above the boat containing the salt under investigation. The couple and millivoltmeter were standardised before and after use at 100° and at the melting points of tin, lead, zinc and sodium chloride, and found to give consistent readings trustworthy to about $\pm 5°$.

Temperature readings were taken every ten minutes (or oftener) throughout the run, and at the end the condensed steam was titrated with $N/10$-sodium carbonate solution and methyl-orange, or, in the case of carbonates, by adding $N/10$-caustic soda solution and back-titrating with $N/10$-sulphuric acid, with phenolphthalein as indicator.

Chlorides, Bromides, and Carbonates.—The table gives the data relative to these salts.

Salt.	Weight (g.).	Temp.	Time (mins.).	Acid produced as c.c. of $N/10$-acid.	Wt. of salt decomposed in 30 mins. (calculated).
Calcium chloride	1·0	970°	30	99·53	0·553
" "	1·0	970	60	154·53	0·428
" "	0·5	812	60	65·5	0·182
" "	0·5	425	60	4·5	0·014
Strontium chloride ...	1·0	970	60	90·9	0·361
" "	0·5	812	60	6·5	0·026
" "	0·5	641	60	4·0	0·016
" "	0·5	638	60	0·5	0·002
Barium chloride	1·0	970	30	7·0	0·073
" "	1·0	970	60	19·1	0·099
" "	1·0	825	30	0·3	0·003
" "	0·5	809	60	Nil.	Nil.
Calcium bromide ...	0·5	690	30	31·6	0·316
" "	0·5	516	30	6·0	0·060
" "	0·5	463	30	4·8	0·048
" "	0·5	348	30	1·2	0·012
Strontium bromide ...	0·5	780	30	20·0	0·248
" "	0·5	575	30	6·2	0·076
" "	0·5	443	30	1·0	0·013
Barium bromide	0·5	770	30	5·0	0·075
" "	0·5	640	30	3·1	0·046
Calcium carbonate ...	1·0	558	45	13·7	0·046
" "	1·0	437	60	5·3	0·013
" "	1·0	390	60	Nil.	Nil.
Strontium carbonate.	1·0	679	60	9·5	0·035
" "	1·0	598	60	5·8	0·022
" "	1·0	455	60	0·3	0·001
Barium carbonate ...	1·0	980	60	38·6	0·190
" "	1·0	684	60	17·1	0·084

Sulphates.—At 970° the sulphates of calcium, strontium, and barium were not appreciably decomposed. From the first sample of barium sulphate used, a trace of sulphuric acid, equivalent to 1·2 c.c. of $N/10$-acid, was produced in the first 5 minutes. This was proved to be due to ferric sulphate present as an impurity.

The production of acid did not continue, there was no evidence of true hydrolytic action, and the residue was not alkaline.

Phosphates.—Calcium phosphate only was examined. This gave no evidence of hydrolytic decomposition even at 970°.

Discussion.

The data recorded above make no claim to great precision, but the authors believe that they may properly be held to justify the following general conclusions.

The chlorides and bromides of calcium, strontium, and barium are all hydrolysed by steam under atmospheric pressure at high temperatures, the ease of decomposition decreasing with increasing atomic weight, the lowest temperature at which it is appreciable being as follows:

Calcium chloride . . .	425°	Calcium bromide	348°
Strontium chloride . . .	640°	Strontium bromide . . .	443°
Barium chloride . . .	970°	*Barium bromide	640°

* Barium bromide appears to be appreciably volatile at 770°.

These figures afford some evidence that the bromides in general are more easily hydrolysed than the chlorides, and, in conjunction with the well-known difficulty of iodide preparation and the work of Fremy and Poulenc (*loc. cit.*) on the fluorides, show that the ease of decomposition for any alkaline-earth metal increases in the order fluoride, chloride, bromide, iodide, whilst for any particular halide it increases in the order barium, strontium, calcium.

In the case of the carbonates of strontium and barium the boat was obviously attacked and this renders the interpretation of the results doubtful. Calcium carbonate evidently decomposes appreciably at 440° in steam and it is interesting to compare this result with the previous observation (Pott, "Studien uber die Dissoziation von Calcium-Strontium- und Barium Karbonat," 1905) that measurable dissociation is observed at 525°.

Qualitative experiments with sodium and potassium nitrates showed that these were largely decomposed at temperatures just under 600°, leaving a strongly alkaline residue in the boat. The gaseous products comprised both nitric acid and oxides of nitrogen, but further investigation of this decomposition was abandoned, as it was likely to require an elaboration of experimental procedure disproportionate to the results anticipated.

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CXVI.—*Studies with the Microbalance. Part III. The Filtration and Estimation of very small Amounts of Material.*

By Ernst Johannes Hartung.

Quantitative micro-analytical work involving precipitation and filtration is beset with considerable difficulty because errors due to adsorption, mechanical loss of material, solubility of precipitates, and accumulation of dust are apt to assume serious proportions in spite of the greatest care on the part of the operator. Moreover, the difficulty of estimating the magnitudes of these errors makes subsequent attempts to correct the experimental results very uncertain. In view of its importance, some preliminary work on the general analytical technique for dealing with 1—2 mg. of material was carried out in this laboratory in 1910 by G. A. Ampt, using the Steele–Grant microbalance. For filtering operations, he employed asbestos in small perforated silica crucibles weighing about 1 g. and transferred the precipitate into them in various ways. The results of his work (unpublished) showed that asbestos was unsuitable as a filtering medium for small amounts of material owing to mechanical and chemical alterations in weight, and that serious losses of precipitate were inevitable in any method of transference from one vessel to another. The obvious remedy is to carry out precipitation in the crucible itself and to adopt reversed filtration through a tube packed with platinum sponge for removal of mother-liquor and washings. Emich ("Mikrochemisches Praktikum," 1924, p. 62) has described such a device for use with 5—10 mg. of material; asbestos is employed instead of platinum sponge and the precipitation vessel with its filtering tube (3—4 g.) is weighed on a Kuhlmann balance to the nearest 0·005 mg. A few examples of analyses are given in which the errors are quoted as usually below 1—2 parts per 1000. As far as the author is aware, however, no general methods for the accurate analysis of amounts of material weighing less than 1 mg. have hitherto been described. When, therefore, the need arose for estimating with precision the composition of very small quantities of mixtures of silver and silver iodide by a procedure involving filtration, the capabilities of the Steele–Grant microbalance were utilised in investigating the conditions for successful quantitative work. The original problem has not yet been solved satisfactorily owing to the great difficulty of separating completely silver iodide from silver, but the methods which have been developed are fairly general in application and may be of use to others who are con-

strained to work with very small amounts of material. The apparatus required consists of a sensitive microbalance (weighing to 10^{-4} mg.), a silica crucible and filtering tube, a dust-free enclosure for carrying out filtration, an evaporator and electric oven, sundry small appliances such as silica pipettes, tubes, etc., and specially prepared reagents.

The Microbalance.—Two Steele–Grant instruments were available, each carrying a load of 100 mg. and weighing accurately to 10^{-4} mg. It was impracticable to work with a crucible and filtering tube which weighed together less than 500 mg. and consequently one of the balances was modified to enable it to carry this load without material reduction in its absolute sensitiveness. In the usual form of the instrument, a constant weight fused to one end of the beam counterpoises a load hanging from a silica fibre attached to the other end. This load consists of a very light rack carrying the object to be weighed, certain small weights and a silica bulb by means of which the beam is equilibrated through alteration of air pressure in the balance case. The bulb constitutes the major portion of the load, since it must be stoutly blown in order to resist deformation with varying external pressure. By removing the bulb from the rack and fusing it to the other end of the beam as part of the constant weight, almost the whole of the load on the fibre is available for the object to be weighed. It is, of course, necessary to determine the displacement value of the bulb in its new position, since the ratio of the lengths of the balance arms now enters into each weighing, but this may easily be done by means of a small known weight, the value of which has been found against the bulb of an unmodified instrument in the usual manner. This procedure was followed with one of the two available balances, and weighings consistent to the nearest 10^{-4} mg. could then be made in a load of 500 mg., or 1 part in 5×10^6 parts. It is perhaps scarcely necessary to remark that, when material other than silica is weighed, certain corrections are required for the difference in density between silica and the material; but for quantities less than 1 mg., these may usually be neglected.

Filtering Apparatus.—The silica crucible in which the analytical operations are conducted is 5—6 mm. in diameter and about 16 mm. in depth (Fig. 1, E), with a capacity of 0·3 c.c. It is provided with two hooks for handling and suspension, the lower of which is shaped to act, in addition, as a support for the filtering tube during weighing so that the point of the tube does not rest on the bottom of the crucible. The tube (Fig. 1, F) is also made from vitreous silica, 30 mm. in total length and 0·3 mm. in bore. It is bent at a right angle in its upper portion and near the lower

end is a constriction above a 3—4 mm. column of platinum sponge. This is made by igniting ammonium chloroplatinate and introduced by suction in water, followed by careful compacting with a platinum wire. The lower orifice of the tube is then somewhat constricted in the oxy-gas flame. A suitable rate of passage of water through the finished filter with strong suction is about 3 c.c. per hour and finely-divided precipitates are completely retained by it. Care must be taken, however, that the filter is never ignited above a low red heat, otherwise the platinum sponge tends to shrink and

FIG. 1.

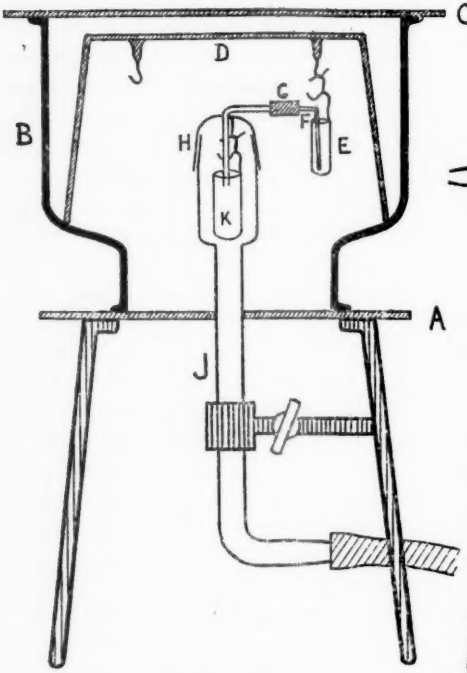
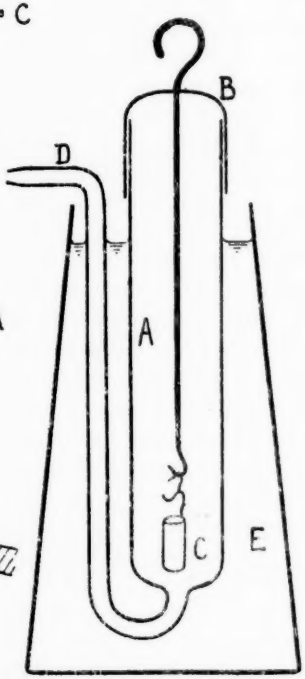


FIG. 2.



may leave channels which impair its filtering quality. Attempts were made to replace the platinum by finely-ground silica, firmly compacted and then sintered together, but shrinkage was so marked that the resulting filters were useless.

The dust-free enclosure in which filtration is carried out is shown in Fig. 1. A ground glass plate, A, with central perforation is cemented with pitch on top of an ordinary tripod with the ground surface upwards. On this rests a glass "dialysing jar" with ground ends, B, about 12 cm. in diameter and 10 cm. deep; this is closed above with the ground glass plate, C. On the ledge

inside the jar stands a light glass framework, D, provided with suitable hooks from one of which the crucible, E, hangs. The filtering tube, F, is inserted in a short length of clean rubber tubing, G, on the end of the arm of the ground cap, H, of a vertically clamped glass tube, J, which passes snugly through the central perforation of the base plate of the chamber. The enlarged upper end of this tube encloses a silica crucible, K, of rather more than 1 c.c. capacity, which hangs from a hook cemented to the inside of the ground cap. By this device, the filtrate from E may be collected in K without contamination or loss. The lower end of the tube J is connected to an exhaust pump or an evacuated receiver during filtration. The crucible E is introduced by means of a bent silica rod after raising C, and the filtering tube is inserted by a pair of narrow-pointed forceps into the moistened end of G after raising B. The tips of these forceps require special preparation; if they are made of smooth metal or ivory, there is great risk of the silica tube slipping out, whilst if the metal is roughened, some of it is gradually transferred to the smooth silica tube where it is visible as greyish weighable stains. This trouble was obviated by arming the tips with good quality calendered writing paper, cemented on with a little varnish and subsequently trimmed to shape with a razor. After placing the filtering tube and crucible in position, they are easily and safely adjusted for filtration by raising or lowering J and sliding B on A. No lubricant is used on any of the ground surfaces except that of the cap H and, if care be taken that none is allowed to soil the interior of the enlarged end of the tube J, the crucible K may be readily introduced or removed without fear of contamination. By means of this apparatus, distilled water and pure concentrated nitric acid may be passed repeatedly from the crucible through the filtering tube without changes in weight greater than 0·0001 mg. Such constancy is not possible, however, if crucible and tube are made of glass, owing to the solubility and hygroscopic character of this substance. For these reasons also, it is advisable to prevent contamination of the filtrate where this is undesirable, by making the ground cap H and its arm from vitreous silica.

Evaporator and Electric Oven.—An evaporator is necessary in which liquids may be evaporated, or kept hot in order to coagulate precipitates, with complete protection from dust. A simple and efficient form is shown in Fig. 2; the wide glass tube, A, is 3·5 cm. in diameter and 18 cm. long and is closed above by a loosely fitting cap, B, carrying a vertical glass rod with a hook from which the crucible, C, hangs. The lower portion is immersed in a glycerol bath, E, regulated in temperature by hand, and a stream of pure

dry filtered air is passed continuously through the tube D. In this way, exclusion of dust is assured and, if the glycerol be kept at 130—150°, aqueous solutions may be rapidly evaporated in a few minutes without loss by boiling or spraying. A small electric oven is used for ignitions up to a dull red heat; it consists of a vertical silica tube sealed at the lower end and surrounded with the usual heating coils and packing. The lid is a silica watch-glass, to the convex lower side of which is sealed a silica hook for suspending the objects to be heated. This cover is provided with a small silica handle and the upper part of the oven is covered with an inverted glass basin as a protection from dust.

Reagents.—Special purification of all reagents was found to be necessary, particularly as regards freedom from dust. Water was twice distilled in a silica apparatus in the usual way and preserved in a capped silica flask. The residue on evaporation corresponded to 1 mg. per litre, which included any dust contamination during the operation and was insignificant as a source of error. Acids, ammonia, and other liquids were distilled immediately before use by heating them in conical flasks and exposing to the vapours the outside of a clean silica test-tube full of water. The condensed drops were removed by an ignited silica pipette, fashioned like a medicine dropper, and either added at once to the crucible, or diluted to the required degree with water in small, covered silica tubes. Solid reagents were obtained by twice crystallising the best commercial analytical reagents in silica vessels, special care being taken to avoid contamination with fibres and dust.

The general technique for carrying out an analysis is as follows: The crucible and tube are cleaned by boiling concentrated nitric acid, washed repeatedly with water, dried over a small alcohol flame, and weighed together. During these operations, the crucible is handled on the end of a silica rod and, when clean, hangs from a silica hook mounted on a cork and protected from dust by a glass cover. After weighing, the filtering tube is removed from the crucible by forceps, the sample introduced, the tube replaced in its support so that the lower end does not come in contact with the sample, and the whole reweighed. The filtering tube is then put in place in the filtering apparatus, and the material in the crucible is dissolved by introduction of one or two drops of the appropriate solvent by a silica pipette, followed by heating, if necessary, in the evaporator. It has been found that even if effervescence takes place during solution, *e.g.*, calc-spar in acid, no loss by spraying occurs owing to the depth of the crucible and the very small amount of gas evolved. The precipitating agent is then added and the crucible is heated in the evaporator until

clotting of the precipitate, or sufficient increase in grain size, has taken place. The crucible is then cooled in the filtering chamber, the liquid removed by the filtering tube, and the precipitate washed. The only satisfactory criterion of complete washing is the constancy in weight of the residue, but three or four applications of a few drops of the washing liquid are usually ample, since the filtering tube removes the liquid completely. Should the tube become choked, making filtration very slow, it may be freed by detaching the vertical tube, J (Fig. 1), from the exhaust pump and blowing into it for a few moments. When washing is finished, the filtering tube is detached from the rubber and placed in its support in the crucible, after its upper end has been rinsed with a drop or two of water. The whole is then dried in the evaporator, ignited, if necessary, and finally weighed. Analogous methods may also be applied to the filtrate in the crucible K (Fig. 1), should further analysis of this be desired.

In order to test the general accuracy attainable with this apparatus, certain standard analyses were performed after the various inherent sources of error in each case had been discovered and guarded against. The results are summarised in Table I, in which

TABLE I.

Estimation of positive radicals in pure salts.

Expt.	Salt.	Weight in mg.	Estimated as	Weight of ppt. in mg.	% of positive radical.	Pure salt requires
1	$AgNO_3$	0·6833	AgCl	0·5763	63·47	
2	,,	0·3994	,,	0·3355	63·22	63·50
3*	,,	0·1877	,,	0·1548	62·1	
4	KCl	0·8895	$KClO_4$	1·6455	52·20	
5	,,	0·7829	,,	1·4529	52·37	52·44
6	,,	0·0965	,,	0·1808	52·9	
7	$Pb(NO_3)_2$	0·9024	$PbSO_4$	0·8242	62·38	
8*	,,	0·8245	,,	0·7498	62·11	62·55
9	,,	0·1649	,,	0·1503	62·25	
10	$BaCl_2$	0·9288	$BaSO_4$	1·0309	65·33	65·94
11	,,	0·2856	,,	0·3173	65·40	
12	$CaCO_3$	0·4469	CaC_2O_4	0·5767	40·38	
13	,,	0·3510	,,	0·4471	39·86	
14	,,	0·1482	$CaCO_3$	0·1474	39·8	40·04
15	,,	0·0878	$CaSO_4$	0·1209	40·5	
16	,,	0·0844	,,	0·1161	40·5	

* Known source of error.

all weights are given in milligrams; they have not been specially selected and are therefore typical of the methods described. Carefully purified and tested salts were used, and the positive radicals were estimated in each case. Inspection of the figures shows that

the analyses are reasonably accurate even for quantities of material as small as 0·1 mg., where the errors in the examples tried have not exceeded 1%, and for larger amounts the errors are usually much less proportionately.

There are several sources of error which, though easily controlled in ordinary routine, are apt to assume serious proportions in micro-analytical work of this kind. The most variable of these is due to accumulation of dust, particularly when the crucible and tube are wet; however, a number of trials has shown that, by reducing to a minimum the time during which the apparatus and reagents are freely exposed, by avoiding agitation of liquid reagents, and by washing down the outside of the pipette with a few drops of water immediately before introducing any liquid into the crucible, errors due to dust are insignificant except when dealing with less than 0·1 mg. of material. Mechanical loss of precipitate is another source of error which has caused some trouble, especially when dealing with very finely-divided precipitates which cannot be made coarse-grained by the usual analytical methods. For example, it is practically impossible to precipitate at boiling temperature without loss in a small crucible with 2 or 3 drops of solution, and the only remedy is fairly prolonged heating after precipitation until the solid settles readily. Further, when washing such a precipitate as calcium oxalate, it is essential to allow the drops of washing liquid to fall into the crucible without forming a bridge between this and the point of the pipette, otherwise some of the solid will spread on the latter and be lost. Errors due to adsorption are also difficult to control and are generally much more serious than in ordinary analytical work, for a fraction of a drop may mean a large excess of reagent. For example, calcium oxalate precipitated with a considerable excess of ammonium oxalate may contain as much as 10% of its weight of the ammonium salt, which cannot be removed by washing; in this case, careful ignition of the precipitate to the carbonate at 400° removes the difficulty completely, but the general remedy is to use dilute solutions of reagents of known concentration. When adsorption cannot be prevented, it is sometimes possible to wash out the adsorbed material after ignition of the precipitate, as with barium chloride on barium sulphate (Pregl, "Organische Mikroanalyse," 1923, p. 147), or to estimate it by some means, as with silver nitrate or silver iodide by evaporation with a drop of dilute hydrochloric acid. The most serious of all sources of error is, however, the solubility of the precipitate, especially in the washing liquid. The reason is that the amount of liquid necessary is out of all proportion to the amount of precipitate, because it is mainly used in washing the interior of

the crucible. It is rarely possible to employ less than 0·5 c.c., which, for 0·5 mg. of precipitate, corresponds to 1 litre per g. and involves a possible error of 1%, if the solubility of the precipitate is 10 mg. per litre. In Table I, Experiment 3 shows the effect of using too great an excess of hydrochloric acid in precipitating silver chloride, owing to increased solubility of the salt. Expt. 8 shows the effect of washing with dilute sulphuric acid, in which lead sulphate has the minimum solubility of 5 mg. per litre, instead of diminishing the solubility still further by addition of alcohol, as in Expts. 7 and 9. Some error due to solubility is inevitable, but it may be diminished by careful regulation of the conditions of precipitation, proper choice of the washing liquid, and strict economy in its use. It is, of course, possible to employ a saturated solution of the precipitate itself for washing, but great care is necessary to avoid introduction of solid particles. This procedure has not been adopted in obtaining the results given in Table I, nor have corrections for any possible sources of error been applied.

The technique described may easily be extended to a large number of micro-analytical problems, provided that these are not too complex. There is, of course, no point in using the microbalance for analysis when sufficient material for the usual laboratory procedure is available, although in some cases, the instrument offers a more accurate and much more expeditious method. For example, the composition of a mixture of sodium and potassium chlorides may be determined rapidly and accurately by evaporating less than 0·5 mg. with a single drop of nitric acid and weighing the mixed nitrates in the residue. Apart, however, from the fact that the chance of accidental error is always greater when dealing with very small quantities, the application of the Steele–Grant microbalance to analytical problems has certain limitations. Volatile liquids cannot be weighed without much trouble, although, when the composition of a liquid is in question, it may be measured with a small pipette. The simplest way to calibrate a pipette for use with the microbalance is to make up an aqueous solution of some stable anhydrous salt (*e.g.*, potassium chloride) of known concentration in the usual manner; a pipette-full of this solution is then evaporated to dryness and the residue weighed on the microbalance. Volatile solids and hydrated salts cannot usually be weighed without special contrivances, and also correct sampling of small amounts of heterogeneous material is extremely difficult. Further, some gelatinous precipitates are awkward to manipulate with the filtering tube owing to the tendency to become impacted in the end of it. Nevertheless, in spite of these limitations, the apparatus and micro-analytical methods here described have a

considerable range of application with accuracy, and it is hoped that they may be of use to other investigators who find it necessary to work with very small amounts of material.

UNIVERSITY OF MELBOURNE. [*Received, February 15th*, 1926.]

CXVII.—*The Ternary System Sodium Thiosulphate–Sodium Sulphate–Water.*

By RICHARD RANDOLPH GARRAN.

THE system sodium thiosulphate–sodium sulphate–water has been examined at 0·8°, 18°, 25° and 40°, the temperature being maintained constant to within 0·02° in the last three cases and to within 0·1° in the first. The transition between decahydrated and anhydrous sodium sulphate in presence of sodium thiosulphate has also been studied.

Mixtures, prepared as indicated in the descriptions of the various isotherms, were rotated in stoppered glass tubes in a thermostat for periods varying from 3 to 24 hours; then, after allowing the solid to settle, a definite volume of solution was drawn off by means of a pipette fitted with a cotton-wool filter and weighed in a tared bottle; the solid was rapidly drained on a Büchner funnel and a portion of it weighed. The solution was diluted and the solid dissolved to known volumes in each case and aliquot parts of these were taken for analysis. The values of the densities of the solutions are probably not accurate beyond two or three units in the third decimal place.

Thiosulphate was determined by adding a known small excess of standard iodine solution and titrating this excess with a solution of sodium thiosulphate the normality of which was obtained from a hydrochloric acid solution (standardised against calc-spar) by means of a mixture of potassium iodide and iodate.

For the determination of the sulphate, the following methods were decided upon after many trials:

(i) The solution was evaporated to dryness with excess of sulphuric acid, and the residue heated to convert it completely into sulphate and to drive off the excess of acid and the sulphur which was formed. From the total weight of sulphate present and the known amount of thiosulphate, the amount of sulphate originally present was readily calculated.

(ii) The solution of thiosulphate was oxidised, by heating with bromine water in the presence of a little alkali, in accordance with the following equation (Mayr and Peyfuss, *Z. anorg. Chem.*, 1923,

127, 123; 1924, **131**, 203): $Na_2S_2O_3 + 4Br_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HBr$. After the excess of bromine had been expelled, the sulphate was precipitated as barium sulphate and the amount of sodium sulphate originally present calculated as above.

(iii) When thiosulphate was present in large excess, method (ii) was found to be untrustworthy. The sulphate present was then precipitated as barium sulphate in cold neutral solution (barium thiosulphate is soluble under these conditions), allowed to settle for 24 hours, and washed three times by decantation, being allowed to settle during 18 to 24 hours each time. The precipitate was then boiled with dilute hydrochloric acid to make it coarser, filtered off, and weighed. This method was found to be trustworthy, but the time required was considerable.

The isotherms at 0·8° and 25° are based entirely on analyses by the first method: that at 18° almost entirely, and that at 40° partly, on the second and third methods. Compositions are expressed as percentages of components by weight, and mixed crystals are indicated in the tables by *M.C.* followed by the formula of the major constituent.

Discussion of Results.

The results obtained at 0·8° and 18° are shown in Tables I and II and are plotted in the usual triangular diagram in Fig. 1. Only the solution curves at 0·8° are shown, as the two systems are of similar general form. Suitable mixtures were prepared from water, pure (A.R.) crystals of sodium thiosulphate pentahydrate and pure commercial (B.D.H.) crystals of sodium sulphate decahydrate, and heated to homogeneity in stoppered tubes which were then rotated in a thermostat for several hours (generally over-night) after the solid had settled out. In a few cases, in solutions containing a preponderance of thiosulphate, it was necessary to seed the mixture in order to induce crystallisation.

In Fig. 1 the curve *ab* denotes solutions in equilibrium with solids along the line *a'b'*, which is so short that it gives only very slight evidence of mixed-crystal formation between $Na_2S_2O_3,5H_2O$ and (possibly) $Na_2SO_4,5H_2O$. The curve *bc* denotes solutions in equilibrium with solids along the line *b''c'*, and here there is definite evidence of mixed-crystal formation between decahydrates. The extent of this at 0·8° and 18° is approximately the same.

The two-phase dried solids along the line *b'b''*, which are in equilibrium with the solution at the condensed triple point *b*, were obtained by prolonged drying of the moist solid on blotting paper in a desiccator over the solution *b* at the temperature of the isotherm. Washing with alcohol resulted in partial dehydration of the crystals.

Table I.

Isotherm at 0·8°.

Solutions.			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·040	4·60	0·00	—	—	$Na_2SO_4,10H_2O$.
1·065	3·13	4·48	36·30	1·08	M.C. $Na_2SO_4,10H_2O$.
1·105	2·31	9·63	35·48	2·25	
1·159	1·88	16·03	31·91	4·95	
1·190	1·87	19·62	34·68	5·41	
1·247	1·56	25·63	32·14	8·38	
—	1·34	30·07	30·10	10·39	
1·312	1·27	32·26	32·84	9·28	
1·324	1·58	33·91	29·10	12·47	*
—	—	—	32·80	14·86	
1·314	1·22	32·72	15·49	36·80	M.C. $Na_2SO_4,10H_2O$ and M.C. $Na_2S_2O_3,5H_2O$.
—	—	—	15·83	39·67	
—	—	—	12·82	44·51	
1·317	1·15	32·77	9·10	45·07	
1·317	1·44	32·72	0·56	61·12	M.C. $Na_2S_2O_3,5H_2O$.
1·315	—	33·57	—	—	$Na_2S_2O_3,5H_2O$.

* Metastable.

Table II.

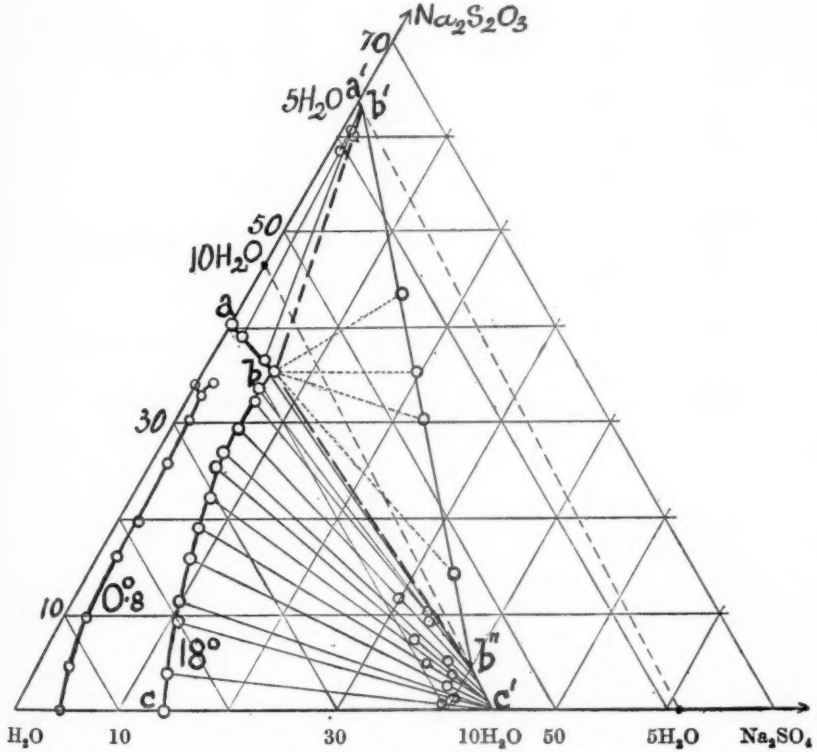
Isotherm at 18°.

Solutions			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·130	14·11	—	—	—	$Na_2SO_4,10H_2O$.
1·150	12·31	4·01	39·21	0·75	M.C. $Na_2SO_4,10H_2O$.
1·180	10·71	9·36	40·14	1·21	
1·194	9·83	11·34	37·22	2·75	
1·225	8·45	15·86	38·75	2·52	
1·248	7·65	19·16	35·84	4·75	
1·276	7·14	22·46	38·64	3·60	
1·301	6·01	25·53	33·34	7·45	
1·314	5·97	27·00	37·59	5·11	
1·338	6·04	29·57	29·66	11·65	
1·356	6·32	32·31	33·92	9·18	
1·374	5·94	33·66	33·20	10·14	
1·390	6·14	35·07	34·12	9·63	
1·399	6·26	35·42	33·40	14·30	M.C. $Na_2SO_4,10H_2O$ and M.C. $Na_2S_2O_3,5H_2O$.
—	—	—	22·64	30·40	
—	—	—	19·40	35·46	
—	—	—	13·99	43·59	
1·394	6·31	35·46	1·02	60·02	M.C. $Na_2S_2O_3,5H_2O$.
1·395	4·87	36·61	0·79	60·73	
1·384	1·65	39·12	0·65	58·54	
1·378	—	40·36	—	—	$Na_2S_2O_3,5H_2O$.

The positions of these solids in the diagram along the line joining the end members, b' and b'', of the two series of mixed crystals provide strong evidence for the existence of the two series.

The isotherm at 40° (see Table III and Fig. 2) also consists of two curves, *ad* denoting solutions in equilibrium with solids along the line *a'd'*, and *df* solutions in equilibrium with solids along the line *d''f'*. Again the larger range is that of mixed crystals at the sulphate end, but at this temperature between anhydrous salts, whilst that showing mixed-crystal formation between $Na_2S_2O_3,5H_2O$

FIG. 1.



Isotherms at 0·8° and 18°.

and (presumably) $Na_2SO_4,5H_2O$, although more extensive than at lower temperatures, is still very small. The dried solids along the line *d'd''* were obtained by washing the moist solid with warm methylated spirit and drying carefully between folded blotting paper. It was found very difficult in this case to remove all moisture from the solid owing to the finely-divided nature of the anhydrous sodium sulphate which was formed. The complexes in this isotherm were prepared by evaporation, under diminished

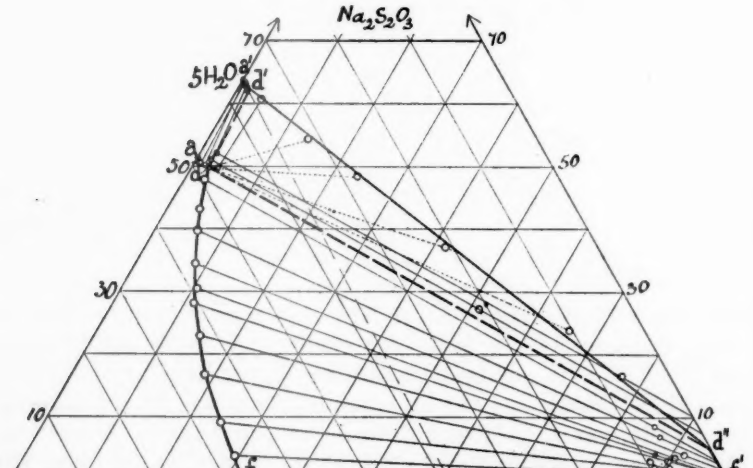
TABLE III.

Isotherm at 40°.

Solutions.			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
—	32·37	—	—	—	Na_2SO_4.
—	29·35	3·79	95·25	0·37	
1·326	24·79	9·06	96·23	0·84	
1·334	18·58	16·73	90·67	1·84	
—	14·76	22·95	90·50	2·87	
1·367	11·14	28·06	87·65	3·98	
—	10·40	30·44	90·85	3·29	M.C. Na_2SO_4.
1·383	8·13	34·35	91·85	3·93	
—	5·90	39·74	86·98	6·80	
1·444	4·28	43·06	81·30	8·81	
1·484	2·46	48·78	85·56	8·29	
—	1·79	51·04	51·47	27·10	*
—	2·03	52·10	76·77	16·38	*
—	—	—	95·33	2·87	
1·496	2·27	49·38	65·72	23·80	
1·496	2·08	49·72	41·80	37·03	M.C. Na_2SO_4 and M.C. $Na_2S_2O_3,5H_2O$.
1·494	2·24	49·73	23·68	48·26	
—	2·09	49·97	13·82	54·14	
—	3·61	49·60	4·06	60·68	*
1·493	2·14	49·88	1·51	62·00	
—	2·45	49·98	0·28	63·41	M.C. $Na_2S_2O_3,5H_2O$.
—	1·58	50·15	0·00	63·26	
1·492	0·67	50·49	0·00	64·58	
1·488	—	51·23	—	—	$Na_2S_2O_3,5H_2O$.

* Metastable.

FIG. 2.

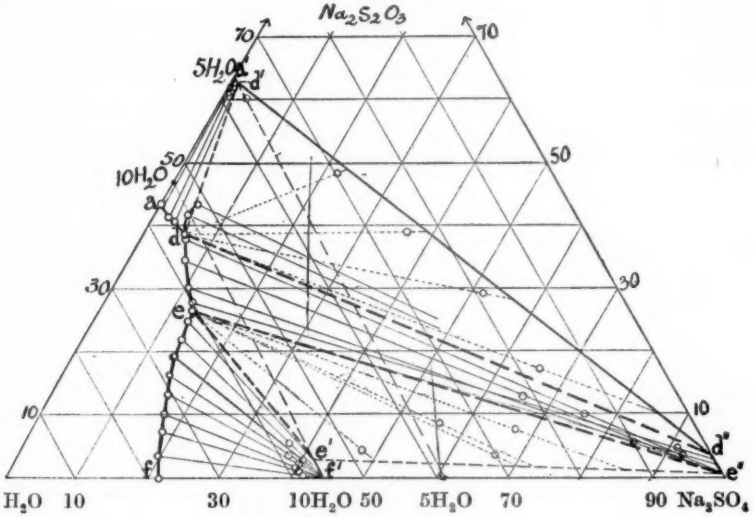


Isotherm at 40°.

pressure, of solutions unsaturated at 40°, using the method employed by Rivett and Lewis (J., 1924, **125**, 1163).

The transition point between decahydrated and anhydrous sodium sulphate will be depressed by the addition of sodium thiosulphate to the solution. With an appropriate mixture in a Dewar flask fitted with thermometer and stirrer, temperature–time curves on heating and cooling were obtained. The mixture was heated at 70° for an hour to hasten the formation of mixed crystals and then cooled to 15°, being well inoculated with crystals of $Na_2S_2O_3,5H_2O$ and $Na_2SO_4,10H_2O$. On slow re-heating, this gave

FIG. 3.



Isotherm at 25°.

a well-defined arrest at 20·30° and on cooling at 19·80°. These temperatures were accurately reproducible, both with the same and with fresh mixtures. The cooling curve was of the usual form, showing undercooling followed by a rise in temperature to the arrest point on seeding. Samples of the solutions in equilibrium with the three solid phases at the arrest points, both on heating and on cooling, were drawn off and analysed, the mean composition being 7·95% of sodium sulphate and 35·0% of thiosulphate. The difference between the two temperatures is probably accounted for by the slow rate of diffusion in the solid phases, the mixed crystals forming above and below the quadruple point being of slightly different compositions. The true transition point should lie between these two temperatures, at about 20·05°.

TABLE IV.

Isotherm at 25°.

Solutions			Wet solids.		
Density.	% Na_2SO_4.	% $Na_2S_2O_3$.	% Na_2SO_4.	% $Na_2S_2O_3$.	Solid phases.
1·204	21·60	—	—	—	$Na_2SO_4,10H_2O$.
1·215	19·74	3·48	41·43	0·34	
1·236	18·44	7·30	40·39	1·06	
1·253	17·12	10·14	39·79	1·56	
1·271	16·13	13·22	39·88	2·23	
1·288	14·86	16·16	37·80	3·50	M.C. $Na_2SO_4,10H_2O$.
1·311	13·97	19·35	40·07	2·94	
—	13·62	22·02	36·85	5·51	
1·359	12·97	24·96	—	—	
—	—	—	47·50	4·44	
—	—	—	66·38	3·60	M.C. $Na_2SO_4,10H_2O$, and
—	12·72	26·86	56·17	8·65	
—	12·72	26·65	67·08	7·77	M.C. Na_2SO_4.
—	13·27	26·12	92·50	3·53	*
1·379	12·15	28·00	91·15	4·70	
—	10·28	30·31	84·66	5·52	
1·401	7·73	34·72	65·45	12·94	M.C. Na_2SO_4.
—	6·06	38·07	75·62	10·08	
—	4·53	41·86	—	—	*
1·453	4·87	43·32	—	—	*
—	5·59	38·83	65·72	17·16	
—	5·66	38·67	51·92	29·11	
1·426	5·64	38·97	36·12	38·99	M.C. Na_2SO_4 and
1·420	5·42	38·85	21·86	48·30	M.C. $Na_2S_2O_3,5H_2O$.
—	5·20	38·96	3·36	60·33	
1·418	4·69	39·45	0·92	61·97	
1·412	3·13	40·92	0·00	63·46	
1·411	2·01	41·53	0·51	61·14	M.C. $Na_2S_2O_3,5H_2O$.
1·410	0·23	43·52	0·22	62·32	
—	—	43·50	(from tables)		$Na_2S_2O_3,5H_2O$.

* Metastable.

The isotherm at 25° should then show three curves, since three solid phases may exist at this temperature. The results obtained are in Table IV and are plotted in Fig. 3. The isotherm consists of three curves: *ad* denoting solutions in equilibrium with mixed crystals along the small range *a'd'* (mainly $Na_2S_2O_3,5H_2O$), *de* denoting those in equilibrium with mixed crystals along the line *d''e''* (mainly anhydrous Na_2SO_4), and *ef*, where the equilibrium is with mixed crystals along *e'f'* (mainly $Na_2SO_4,10H_2O$). The solids along *e''e'* were dried on blotting paper and those along *d'd''* were washed with spirit.

The existence of mixed crystals of decahydrates of the two salts and of a very small range of pentahydrates is clearly shown. The evidence obtained here for the series of mixed crystals of anhydrous salts is not definite, but the work at 40° points to the existence of an analogous series at 25°. The solutions in this isotherm were prepared by dissolving the salt constituent which should mainly

constitute the solid phase in the total amount of water required, then adding the other salt, and rotating the tube in the bath.

The sodium sulphate solution curve has been extended into the metastable region at 0·8°, 25° and 40°, and in each case it shows a decided increase in curvature. If the metastable solution curve in a system where mixed crystals are formed could be fully realised, it should form a closed loop, and this is indicated by the shapes of the curves in the metastable region.

Summary.

1. The system sodium thiosulphate–sulphate–water has been examined at 0·8°, 18°, 25°, and 40°.

2. The existence has been demonstrated of a very short series of mixed crystals of pentahydrates at all four temperatures; of a series of decahydrates at 0·8°, 18°, and 25°; and of a series of anhydrous salts at 25° and 40°.

3. The quadruple point at which four phases co-exist, three being mixed crystals and one a solution, is at a temperature very close to 20°.

The author is indebted to Professor A. C. D. Rivett for suggesting this work and for advice during its progress.

UNIVERSITY OF MELBOURNE. [*Received, February 9th*, 1926.]

CXVIII.—*The Ternary System Sodium Sulphide–Sodium Sulphate–Water.*

By ARTHUR ROBERT HOGG.

THE fact that anhydrous sodium sulphite and sulphate, and their corresponding hydrates, crystallise together within limits (Rivett and Lewis, *Rec. trav. chim.*, 1923, **42**, 954; J., 1924, **125**, 1156, 1162) suggested an inquiry into the relations between sodium sulphide and sodium sulphate. This has been carried out at each of the five temperatures 0·1°, 18°, 25°, 31° and 40°, the complete ternary system being described in each case.

For the most part the salts used have been of analytical reagent (B.D.H.) standard. Mixtures of these and water in varying amounts have been brought to equilibrium in rubber-stoppered glass tubes, the proportions taken being such that about 6% of the total was present as solid when equilibrium was attained. Three methods of attaining equilibrium were employed: (i) cooling homogeneous solutions from higher temperatures, inoculating, if necessary, with

the appropriate solid phase (systems at 0·1° and 18°): (ii) heating heterogeneous mixtures from lower temperatures (systems at 25° and 31°): (iii) evaporating homogeneous solutions under reduced pressure at the temperature of experiment until sufficient solid appeared (system at 40°). When all phases were present, the tubes were mechanically rotated in a thermostat for from 4 to 40 hours.

The second method is satisfactory in giving the course only of the solution curves: it will not give accurate information as to compositions of solid phases, but it sufficed in the cases where it was used. The third method was carried out in tubes fitted with vertical side limbs and connected in batches of six with a small cooled receiver exhausted to about 40 mm. pressure. The tubes were clamped horizontally to a tilting platform in the bath and were gently rocked during the evaporation, which generally occupied about 3 hours. In order to avoid possible loss of hydrogen sulphide, the mixtures were kept in connexion with the pump for as short a time as possible, the vacuum being maintained by condensation. The distillate from six tubes was collected and tested for sulphide. The amount found, part of which was due to priming, was insufficient to affect the analyses appreciably. When sufficient solid had separated, the vacuum was broken and the rocking continued for from 2 to 12 hours.

On attainment of equilibrium, a sample of the solution was withdrawn in a pipette (suitably heated or cooled) through a cotton-wool plug, and weighed. Densities so obtained are correct to one or two units in the third decimal place. Dilution to an appropriate extent gave the solution which was analysed. The moist solid was obtained by rapid filtration on a Büchner funnel and a weighed amount was dissolved to a known volume. In some cases, the wet solid was washed with alcohol and dried between folds of blotting paper. In analysis, sulphide was determined by titration against standard acid, with phenolphthalein as indicator, and sulphate was determined gravimetrically as barium sulphate.

Discussion of Results.

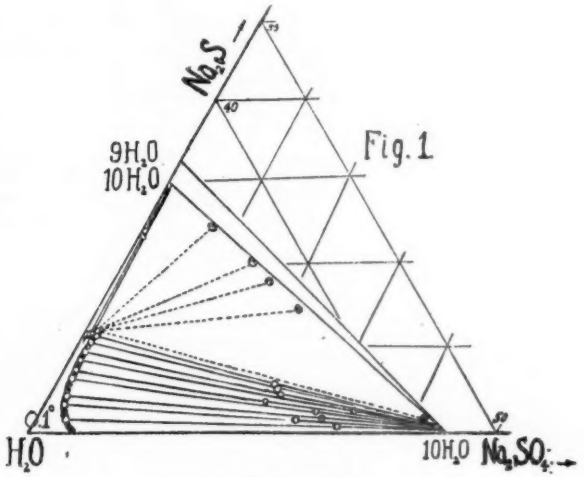
The experimental results are given in Tables I to VI. Compositions are expressed in % of anhydrous salt by weight. In the last column, mixed crystals are indicated by M.C. followed by the formula of the major constituent.

The first point to be noted is that at 0° sodium sulphide has been obtained as a decahydrate, a form apparently not hitherto described. Analysis of the solid, after washing with alcohol and drying with blotting paper, gave Na_2S, 30·04% : $Na_2S,10H_2O$ requires 30·23 and $Na_2S,9H_2O$ requires 32·49%. In the ternary system at 0·1° the

TABLE I.

Isotherm at 0·1°.

Solutions. % by weight.			Wet solids. % by weight.		
D_4°.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·122	11·33	—	30·0	—	
1·125	11·34	0·63	23·4	0·12	M.C.
—	11·22	0·93	23·1	0·43	$Na_2S,10H_2O$.
1·137	11·94	1·16	—	—	
1·131	11·21	1·23	29·6	0·96	
1·130	11·14	1·25	25·1	7·30	M.C.
1·131	11·23	1·19	21·1	13·54	$Na_2S,10H_2O$
1·129	11·16	1·16	18·49	16·53	and
1·129	11·18	1·23	18·34	16·53	M.C.
1·132	11·23	1·18	14·49	21·0	$Na_2SO_4,10H_2O$.
1·129	11·11	1·19	0·47	43·2	
1·124	10·77	1·24	5·56	23·6	
1·110	9·49	1·27	4·49	24·2	
1·099	8·32	1·28	2·59	33·5	
1·091	7·36	1·48	3·60	23·6	M.C.
1·081	6·16	1·54	2·48	28·9	$Na_2SO_4,10H_2O$.
1·066	4·79	1·68	1·64	30·6	
1·052	3·16	2·11	1·49	27·5	
1·041	1·44	2·99	0·45	32·5	



Isotherm at 0·1°.

solution curve for this decahydrate is short (see Fig. 1), but there is definite indication of the separation of mixed crystals containing a very little $Na_2SO_4,10H_2O$.

At the sodium sulphate end the mixed-crystal formation is greater, the limiting member of the series containing 42% of sulphate and 1·5% of sulphide. The points in Fig. 1 marked by crosses within

circles represent mixtures of two solid phases in equilibrium with the solution at the intersection of the two solution curves. The solids were obtained almost free from mother-liquor by washing with alcohol and drying with blotting paper. It will be seen that they all lie very near to the line joining the end corresponding to mixed crystals of (mainly) $Na_2SO_4,10H_2O$ containing sulphide and the point representing the composition $Na_2S,10H_2O$. This gives independent proof of the existence of a decahydrate of the sulphide.

Between it and the nonahydrate in the binary system the transition point has been shown by the cooling method to be 4·7°, the saturated solution then containing 12·46% of sodium sulphide and having a density of 1·128.

TABLE II.

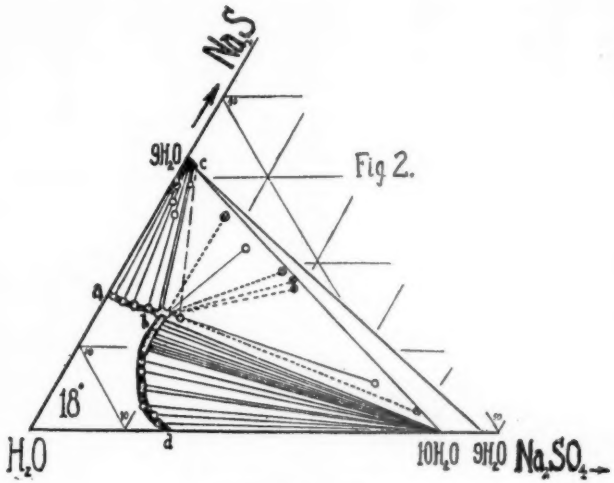
Isotherm at 18°.

Solutions.			Wet solids.		
	% by weight.		% by weight.		
$D^{18°}_{4°}$.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·169	15·95	—	—	—	$Na_2S,9H_2O$.
—	15·65	0·53	30·40	0·32	
—	15·33	2·28	29·27	0·63	
1·187	15·08	3·47	28·15	1·11	M.C.
1·197	14·50	5·20	25·96	2·13	$Na_2S,9H_2O$.
1·212	14·02	5·83	31·56	0·74	
—	13·98	6·44	30·10	1·66	
—	—	—	25·56	7·61	
1·212	13·90	7·21	22·23	11·91	
—	—	—	19·31	17·54	M.C.
1·210	13·95	7·24	18·38	18·91	$Na_2S,9H_2O$
—	—	—	16·93	19·49	and
1·205	13·84	7·22	5·12	33·99	$Na_2SO_4,10H_2O$.
1·210	13·98	7·23	2·56	40·28	
—	13·78	7·16	0·65	42·91	
1·225	13·15	9·75	31·50	1·75	
1·208	13·08	7·01	4·12	32·11	
1·195	12·46	7·00	2·93	35·21	
1·186	12·14	6·93	3·62	32·98	
1·180	11·16	6·79	—	—	
1·175	10·91	6·96	2·08	37·68	
1·169	10·33	7·19	2·35	35·61	
1·167	10·04	7·17	3·13	32·89	
1·165	9·96	7·09	1·04	40·70	
1·162	9·47	7·15	2·20	35·82	$Na_2SO_4,10H_2O$.
1·149	7·99	7·64	1·82	35·84	
1·143	6·82	8·09	1·88	33·39	
1·132	5·33	9·05	1·32	34·65	
1·130	4·54	9·30	0·93	36·79	
1·131	2·84	10·67	0·54	37·27	
1·126	1·51	11·91	0·37	36·05	
1·126	0·62	13·31	0·15	36·17	

At 18° (Table II) the solid separating at the sulphide end is the ordinary nonahydrate containing some dissolved sulphate (see

Fig. 2). Whether the latter is there with water in the same molecular proportion of 1 : 9 cannot be stated. At the sulphate end, however, there is no indication of any appreciable solubility of sodium sulphide in $Na_2SO_4,10H_2O$. It would seem that $Na_2S,10H_2O$ cannot exist in mixed crystals at 18°, while the nonahydrate of the sulphide is insoluble in the decahydrate of the sulphate.

There is no appreciable mixed-crystal formation at 25° or 31° (Tables III and IV) either in the hydrated or anhydrous sulphate



Isotherm at 18°.

TABLE III.

Isotherm at 25°.

Solutions.			Wet solids.		
	% by weight.		% by weight.		Solid phases.
$D_4^{25°}$.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	
1·183	17·86	—	31·68	—	
1·202	17·17	3·40	31·73	0·27	$Na_2S,9H_2O$.
1·205	16·61	5·01	31·76	—	
1·229	15·84	7·18	27·73	13·10	$Na_2S,9H_2O$
1·224	15·89	6·87	23·43	25·89	and
1·221	16·07	6·32	14·35	46·86	Na_2SO_4.
1·228	14·68	8·06	2·58	79·29	
1·222	12·68	10·80	0·61	93·18	Na_2SO_4.
1·237	11·21	12·56	0·13	96·78	
1·241	10·04	14·51	0·99	90·79	
1·240	9·96	14·70	0·57	65·25	Na_2SO_4 and
1·241	9·96	14·67	0·44	48·28	$Na_2SO_4,10H_2O$.
1·204	4·40	17·12	0·35	40·98	
1·203	3·27	17·84	0·49	37·76	$Na_2SO_4,10H_2O$.
—	1·63	19·71	0·47	35·80	

TABLE IV.

Isotherm at 31°.

Solutions.			Wet solids.		
	% by weight.		% by weight.		
D_4°.	Na_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·202	20·60	—	31·42	—	$Na_2S,9H_2O$.
1·210	20·44	1·05	32·44	0·05	
—	19·57	3·04	29·64	0·87	
1·213	19·46	4·11	31·26	1·77	$Na_2S,9H_2O$ and Na_2SO_4.
—	19·66	4·41	30·41	5·47	
1·229	19·33	4·04	27·41	14·89	
1·222	19·69	4·32	20·39	35·73	
1·228	19·42	4·20	11·47	63·46	
1·253	22·22	2·56	3·01	86·41	Na_2SO_4.
1·214	18·69	4·79	3·57	82·00	
—	16·36	6·58	3·59	79·98	
1·214	14·39	8·59	2·19	86·79	
1·219	12·14	11·56	1·96	88·01	
1·228	9·83	14·46	1·27	89·72	
—	7·47	18·92	0·45	92·39	
1·248	6·97	19·47	1·37	85·68	
1·264	4·81	23·06	1·99	68·91	
1·288	2·85	27·39	0·34	84·30	Na_2SO_4 and $Na_2SO_4,10H_2O$.
1·290	2·31	28·65	0·15	64·25	
1·291	2·43	28·72	0·25	42·85	$Na_2SO_4,10H_2O$.
1·294	1·47	29·15	0·27	41·88	
1·285	0·40	29·97	0·05	41·81	

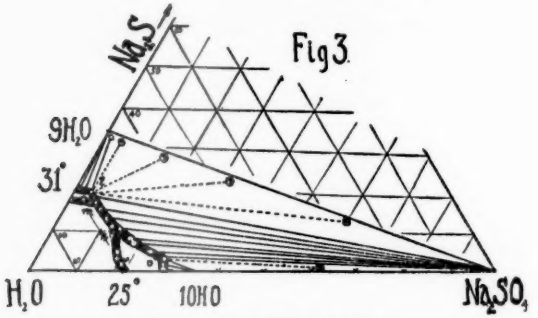


Fig 3.

Isotherms at 25° *and* 31°.

solid phase. The relations are shown in Fig. 3 and need no discussion. At 40°, where only anhydrous sulphate can exist, there is again no discernible miscibility. At all three temperatures, the part of the system in which solid sulphide appears is so small that one cannot make definite assertions about the solid phase.

By the determination of temperature–time curves in slow cooling and heating of suitably chosen mixtures, the transition points were determined as set out in Table VI, together with the compositions of saturated solutions in equilibrium with the solids indicated in the

TABLE V.

Isotherm at 40°.

Solutions.			Wet solids.		
	% by weight.		% by weight.		
$D_4^{40°}$.	N a_2S.	Na_2SO_4.	Na_2S.	Na_2SO_4.	Solid phases.
1·248	25·09	—	31·04	—	
1·248	25·01	—	32·23	—	
1·238	24·06	0·49	32·37	trace	$Na_2S,9H_2O$.
1·238	23·93	0·88	32·94	0·05	
1·256	24·28	1·62	32·08	1·58	
—	23·44	1·77	31·75	2·96	
1·248	23·72	1·90	31·25	5·63	$Na_2S,9H_2O$
1·247	23·79	1·84	30·53	6·69	and Na_2SO_4.
1·253	23·62	1·90	27·57	16·59	
1·253	23·57	1·84	2·08	91·46	
1·241	23·25	1·79	1·69	93·25	
1·223	23·04	1·91	1·89	48·98	
—	22·30	1·94	3·04	86·67	
1·233	21·91	2·44	—	—	
1·233	21·99	2·45	2·39	87·39	
1·239	21·27	2·79	4·14	81·48	
1·228	20·91	3·04	2·28	89·18	
1·233	20·36	3·41	1·76	91·62	
—	14·08	25·22	0·78	95·43	Na_2SO_4.
1·223	15·45	6·53	—	—	
—	14·97	7·37	1·90	89·62	
1·223	14·25	8·72	3·33	75·75	
1·220	14·31	8·17	—	—	
1·236	9·78	14·14	2·07	81·18	
—	9·49	15·23	1·89	82·58	
1·260	6·18	20·25	1·83	75·63	
—	3·56	24·43	0·78	80·90	
1·302	1·32	28·90	0·18	83·71	

TABLE VI.

Transition points.

Transition.	Temp.	% by weight in soln. Na_2S.	% by weight in soln. Na_2SO_4.	$D_4^{40°}$.
Binary.				
$Na_2S,10H_2O \rightleftharpoons Na_2S,9H_2O$.	4·7° (h) 4·7 (c).	12·46	—	1·128
Ternary.				
Same in satd. Na_2SO_4.	2·3 (h) 2·3 (c)	11·49	1·40	1·135
Ternary.				
$Na_2SO_4,10H_2O \rightleftharpoons Na_2SO_4$ in satd. Na_2S.	20·9 (h) 20·2 (c)	13·41	9·48	—
?	29·6 (h)	19·97	4·48	1·331
—	29·6 (c)			

(h) = arrest on heating. (c) = arrest on cooling.

first column. Sulphate lowers the transition point between deca- and nona-hydrates of the sulphide from 4·7° to 2·3°, whilst the transition point between decahydrated and anhydrous sulphates

may be reduced by sulphide from 32·4° to 20·6°. For small concentrations of sodium sulphide, the depression of this transition point has been measured and found to be directly proportional to the concentration of sulphide. It may be expressed by $D = 0{\cdot}625C$, where D is the depression and C the concentration of sulphide in g. per 100 g. of solution.

A curious arrest at 29·6° (Table VI) has not been explained. The solution has a high density and the arrest may correspond with the formation of a metastable hydrate no trace of which was found in the work on the 31°-isotherm.

Summary.

1. The system sodium sulphide–sulphate–water has been investigated between 0·1° and 40°.

2. Sodium sulphide has been found to form a decahydrate which has not been previously described. The transition point in the binary system between deca- and nona-hydrates is 4·7°.

3. Mutual miscibility is shown by the solid decahydrates of sulphide and sulphate at 0·1°.

4. At 18°, $Na_2S,9H_2O$ can dissolve sulphate (as nonahydrate?) but neither $Na_2SO_4,10H_2O$ nor Na_2SO_4 shows appreciable tendency to include sulphide in its crystals.

5. The transition point between deca- and nona-hydrated sulphides is lowered in the ternary system by sulphate to 2·3°; while that between decahydrated and anhydrous sulphate is lowered by sulphide to 20·6°.

The author's best thanks are due to Professor A. C. D. Rivett for suggesting this investigation and for much helpful criticism.

UNIVERSITY OF MELBOURNE. [*Received, February 22nd,* 1926.]

CXIX.—*The Constitution of Maltose.*

By JAMES COLQUHOUN IRVINE and IAN MACLEOD ARMSTRONG BLACK.

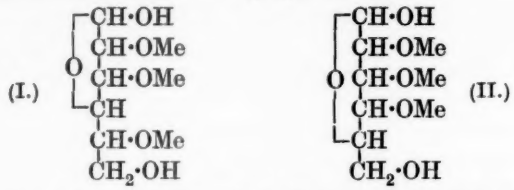
A CONSIDERABLE section of the work conducted in this laboratory on the constitution of polysaccharides has been withheld from publication for some years owing to the fact that the results could not be readily explained. As these discordant features accumulated, it became increasingly evident that current views regarding the structure of maltose required revision and that it was necessary to

study the problem anew. This we have done and, as our results differ fundamentally from those upon which the accepted structure for the disaccharide is based, it is desirable to review the whole situation.

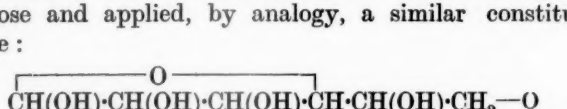
The first attempt to solve the constitution of maltose by means of methylation was made by Purdie and Irvine (J., 1905, **87**, 1022), who applied the silver oxide reaction directly to the free sugar. Although the alkylation was complicated by oxidation of the reducing group, the decisive result emerged that, on hydrolysis of the product, crystalline tetramethyl glucose was produced. This revealed the structure of one-half of the maltose molecule which, on the basis of the amylene-oxide formula for glucose,* becomes:

$$CH_2(OH)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH\text{—}O\text{—Reducing glucose residue.}$$
$$\qquad\qquad\qquad

glucose (I), but adopting meanwhile the amylene-oxide structure, it may be termed 2 : 3 : 4-trimethyl glucose (II).

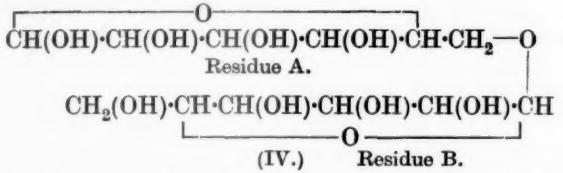


Irrespective of the oxygen-ring, the essential point is that the formation of such a sugar implies that the two hexose residues in the disaccharide are coupled through a terminal hydroxyl group. On this basis, Haworth and Leitch ascribed the following structure to maltose and applied, by analogy, a similar constitution to melibiose :



(III.)

This formula has remained in use for the past seven years, but was modified recently (Charlton, Haworth, and Peat, this vol., p. 89) by the incorporation of an amylene-oxide linkage in each glucose residue, giving the structure :



(IV.) Residue B.

Evidently the constitution as given above is valid only if each half of the molecule gives rise to the appropriate methylated glucose. With regard to residue B, this was already known from the results of earlier workers, and the additional experimental evidence contributed by Haworth and Leitch consisted in the isolation and identification of the trimethyl glucose derived from residue A. Considering the fundamental structural issues involved (which are by no means confined to maltose), it is of the utmost importance to know that the trimethyl glucose is actually what it was described to be. Our results, unfortunately, show that this is not the case. The trimethyl glucose obtained by us from maltose is the crystalline 2 : 3 : 6-isomeride, and not, as stated by Haworth and Leitch, the liquid 2 : 3 : 4-variety. The erroneous conclusion to which the latter workers came is in no way concerned with the position of the oxygen

ring in glucose or with a difference in the interpretation of results, but is attributable to failure to identify correctly the sugar actually formed. It is regrettable that correction should have been so long delayed, particularly as the constitutional formulæ of other disaccharides and of the polysaccharides based on glucose become involved in the fundamental error.

The evidence upon which Haworth and Leitch identified and ascribed a structure to the trimethyl glucose they obtained from maltose may be discussed. The sugar failed to solidify and was separated from tetramethyl glucose by distillation, a process of doubtful utility in any case where the presence of 2 : 3 : 4-trimethyl glucose might be expected. No crystalline derivative was prepared and the bulk of the material was subjected to oxidation by nitric acid, the product thus formed being described as a trimethyl saccharolactone since it corresponded in composition with such a compound. Inquiry into the particular method of oxidation employed has, however, shown that it is untrustworthy. We have ascertained that unchanged sugar may persist along with oxidation products and, in addition, the removal of nitric acid by evaporation with alcohol results in partial esterification of the oxidation acids. In consequence, the analytical results obtained on *undistilled* products are subject to serious errors. For example, a methyl group may be removed by oxidation from the terminal 6-position of the sugar chain, but an ethyl group may enter the carboxyl position, thus introducing compensation into the methoxyl determinations. We have encountered all of the above complications and may cite the oxidation of monomethyl glucose by nitric acid as a conspicuous, but by no means unique, example of a complex reaction which leads to a mixture of products displaying fortuitously the properties and composition of a simple lactone. This accounts for our recent practice in isolating oxidation products in the form of volatile esters or of crystalline derivatives.

Turning to other properties of the trimethyl glucose described by Haworth and Leitch, it may be mentioned that the specific rotations of the compound did not agree with those determined by previous workers (Irvine and Dick, *loc. cit.*) and failed to reveal the characteristic depression shown after distillation. Information was, in fact, available showing that it is impossible to identify 2 : 3 : 4-trimethyl glucose by observation of the activity of distilled specimens, as the value of the specific rotation may vary as much as 20° to 30° owing to the partial transformation of the dextrorotatory sugar into its lævorotatory anhydride. This irregularity was encountered so far back as 1903 and was again emphasised by Irvine and Oldham (J., 1921, **119**, 1754).

Consideration of the whole situation shows that the claims of Haworth and Leitch regarding the trimethyl glucose they obtained from maltose rested upon insecure experimental evidence which has not been supplemented as knowledge of methylated sugars increased. There can be no doubt that the material they described as the liquid form of trimethyl glucose was an impure specimen of the 2 : 3 : 6-isomeride, which failed to crystallise owing to the experimental treatment to which it had been subjected. In this connexion, Irvine and Hirst (J., 1922, **121**, 1214) state "the capacity of this sugar (2 : 3 : 6-trimethyl glucose) to separate in the solid form is seriously affected by impurities and seems to be inhibited by thorough drying so that, on distillation, a viscous syrup is obtained which solidifies only after several weeks. Even gentle warming above the melting point is sufficient to impair crystallisation." The above statement, taken in conjunction with our experience of oxidations by means of nitric acid, shows that it is hazardous, without the most exhaustive confirmation, to claim that any preparation of a trimethyl glucose which fails to crystallise is the 2 : 3 : 4-isomeride.

In overturning a result upon which so many other constitutional formulæ depend, it has been necessary to exclude sources of error so far as they can be foreseen and to repeat the operations several times and by independent workers. Reference is made in the experimental part to some of the precautions adopted and to variations in the procedure. These fall under three main heads: (1) confirmation of the purity and uniformity of the maltose used, (2) variations in the method of methylation, (3) alternative methods of isolating the scission products. We employed three distinct samples of maltose, one of which was made in the laboratory during the War and was certified as conforming to bacteriological standards. With regard to the process of methylation, we followed in the first instance exactly the method described by Haworth and Leitch, applying the methyl sulphate reaction to the free sugar. In other experiments, methyl sulphate was used only until the product was soluble in chloroform, the methylation being completed by the silver oxide reaction alone. Despite these experimental variations, the same result was obtained, the product on isolation being a viscous syrup showing the properties ascribed by Haworth and Leitch to heptamethyl methylmaltoside.

It may be mentioned, however, that the methoxyl and carbon values determined on this material were consistently low, and that satisfactory analytical figures were obtained only when the initial material consisted of crystalline methylmaltoside. The hydrolysis proceeded normally, the liberated sugars being separated by extrac-

tion of an aqueous solution with chloroform. By this means it was possible to effect a sharp separation of the tetramethyl and trimethyl glucoses without distillation or heating above the melting points of these compounds. In all the experiments, both sugars crystallised and proved to be respectively 2 : 3 : 4 : 6-tetramethyl glucose and 2 : 3 : 6-trimethyl glucose. As a precautionary measure, we examined all the hydrolysis products to ascertain if any 2 : 3 : 4-trimethyl glucose was present, but no trace of this sugar could be detected.

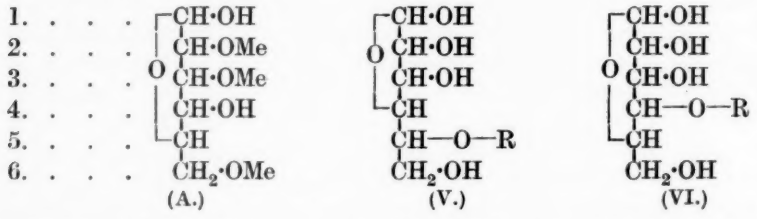
In order to place our procedure beyond question, we have duplicated the entire research, using pure β-methylmaltoside as the starting material. In this case also, the methylation was conducted in two ways, using either the silver oxide method or the methyl sulphate reaction throughout. Here again the same result was obtained, irrespective of the method employed, the hydrolysis of the compound giving, as before, crystalline tetramethyl glucose together with crystalline 2 : 3 : 6-trimethyl glucose free from the liquid isomeride. Finally, for the purposes of the present investigation, Irvine and Oldham prepared 2 : 3 : 4-trimethyl glucose by synthetical operations designed to leave the terminal $CH_2 \cdot OH$ group unsubstituted (J., 1925, **127**, 2729). The product was entirely different from the isomeride obtained from maltose.

Considering the precautions adopted and the results of collateral investigations designed to test sources of error, we are convinced that maltose cannot be formulated in either of the ways suggested by Haworth. The necessity for correction is not limited to the single case of maltose, but extends to all constitutional schemes in which the maltose structure is either directly or indirectly involved. For example, with the displacement of maltose from the position it has hitherto occupied in the structural classification of the disaccharides, the following constitutional relationships must be again regarded as conjectural: (1) maltose and cellobiose, (2) maltose and gentiobiose, (3) lactose and melibiose (Haworth and Leitch, *loc. cit.*; J., 1918, **113**, 188; Haworth and Hirst, J., 1921, **119**, 193; Haworth and Wylam, J., 1923, **123**, 3120).

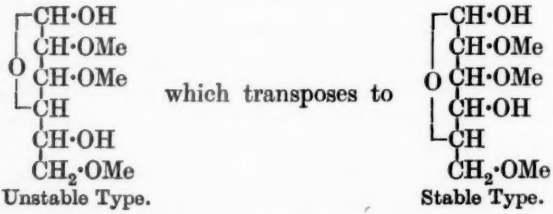
Further, speculations on the structure of *iso*maltose and of the molecular unit of starch, which have naturally been founded on a constitutional formula for maltose, lose their significance, a conclusion foreshadowed by results obtained in this laboratory on the methylation of starch and of the polyamyloses.

It would be premature, even with the additional information now available, to speculate as to the alterations in disaccharide formulæ which are now necessary, and discussion is limited to some general considerations. The question arises as to whether methylation

alters the linkage of one sugar residue with another, but this has already engaged our attention (Irvine and Oldham, J., 1925, **127**, 2910), although the argument that maltose and cellobiose give rise to different methylated sugars no longer holds. There remains an analysis of how far conclusions as to structure are logically valid when based on the formation of 2 : 3 : 6-trimethyl glucose. This sugar, formulated as an amylene-oxide, may be represented as (A) and on first inspection it might appear that all disaccharides which yield this compound must have the glucose residues attached through position 4. But inspection will show that the number of diglucoses which qualify for this mode of linkage is now larger than stereochemical considerations accommodate. The situation thus created is disconcerting, but is greatly simplified when it is recognised that 2 : 3 : 6-trimethyl glucose is capable of reacting as a γ-sugar, this property of the compound having been already pointed out (Irvine and Hirst, *loc. cit.*). It follows that the production of 2 : 3 : 6-trimethyl glucose is not absolutely diagnostic in discriminating between positions 4 and 5 as the point of union of two glucose residues. Thus, if we imagine two disaccharides to be constituted as under (V and VI), where R represents the non-reducing hexose residue,



only the compound corresponding to (VI) would yield the stable form of trimethyl glucose directly. The other could, however, do so indirectly, giving in the first place :

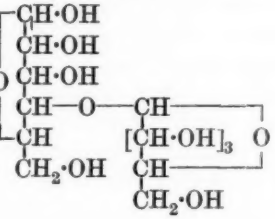


The possibility thus revealed invests all such constitutional studies with precisely the same uncertainty as is encountered in the hydrolysis of sucrose and inulin. Evidently the disaccharides must be studied afresh in the light of the possibility that γ-oxidic or other

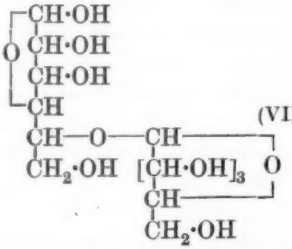
linkages may be present in one or other of the constituent sugars. These considerations have been made the subject of other investigations now in progress in this laboratory.

According to the evidence now submitted, maltose may be formulated either as:

(VII.)



(VIII.)



The methylation process does not discriminate between these alternatives, one of which must represent cellobiose and *iso*cellobiose, whilst the other must be reserved for maltose together with, presumably, *iso*maltose. The conversion of methylmaltoside into β-methylglucoside appears to favour the allocation of formula (VII) to maltose but, on the other hand, the degradation of maltose is more easily explained in terms of formula (VIII). Work is in progress to decide between the above alternatives.

The results now contributed serve to emphasise a view formerly expressed (Irvine, J., 1923, **123**, 898) that no claim for finality can be made regarding the constitution of sugars and that each successive modification represents only a stage in knowledge.

Experimental.

Methylation of Maltose.—In order to economise description, it may be stated that each method of alkylation now described was applied to three distinct specimens of maltose. Two of these were obtained from trustworthy manufacturing firms and were selected as they displayed the correct melting point and specific rotation for the disaccharide. The third specimen was prepared in this laboratory during the War and was subjected, before use, to a special bacteriological examination. It was presumably identical with the material used by Haworth and Leitch. The descriptions of the methylation now given apply therefore to six distinct preparations, and the results quoted are typical.

Method I. The directions given by Haworth and Leitch (*loc. cit.*, pp. 813—814) were adhered to in every detail. After three methylations by means of methyl sulphate, the product extractable with chloroform weighed 27·5 g. (from 30 g. of maltose) and contained 50·5% of methoxyl. On distillation, 19·5 g. of a viscous syrup were

obtained (b. p. 189—191°/0·2 mm.; n_D 1·4685), but it may be noted that a small fraction of lower boiling point was also collected and that a viscous residue remained undistilled. The main fraction, on redistillation, boiled at 190°/0·2 mm. and showed $[\alpha]_D$ in alcohol + 91·1° for $c = 1·15$; $[\alpha]_D$ in acetone + 92·1° for $c = 1·256$; OMe, 50·4%; n_D 1·4706. After another methylation, the product was separated on distillation into three portions, and, although the boiling point showed no variation, the second fraction (11·2 g.) was selected as being in best agreement with the constants quoted by Haworth and Leitch for heptamethyl methylmaltoside.

The methoxyl content was nevertheless slightly low, but purification was effected by solution in light petroleum and extraction with water. A small amount of discoloured syrup was retained in the hydrocarbon solvent, and the main product, when recovered from the water, was entirely decolorised by boiling in chloroform solution with norit. Average yield, 10 g. per 30 g. of maltose used. Found: C, 52·3; H, 8·6; OMe, 52·7. Calc. for heptamethyl methylmaltoside, $C_{12}H_{14}O_3(OMe)_8$, C, 52·9; H, 8·4; OMe, 54·6%; n_D 1·4691; $[\alpha]_D$ in acetone + 90·6° for $c = 1·16$. The maltose provided by manufacturing firms gave results corresponding closely with those described above, although the final yield of methylated maltoside was invariably smaller. The same tendency for the methoxyl value to be low was again observed, successive preparations showing OMe, 52·0 and 52·4, in place of the calculated value 54·6%.

Method II. The initial stages in the methylation were conducted as before and the product soluble in chloroform was isolated. Thereafter only the silver oxide method was applied, the following being an account of a typical case. 40 G. of the partly methylated maltoside were alkylated as usual with methyl iodide (6 mols.) and silver oxide (3 mols.), the treatment being continued for 8 hours. The yield of distilled material amounted to 32 g., of which 22 g. were collected at the boiling point of heptamethyl methylmaltoside. The undistilled residue was rejected and the distilled material was again methylated and fractionated. Finally, the middle fraction was redistilled and purified by solution in light petroleum and extraction with water as already described.

The heptamethyl methylmaltoside thus isolated was identical with that obtained by Method I and gave the same hydrolysis products, but the methoxyl content was again low (OMe, 52%) and the refractive index was 1·4700 in place of 1·4691.

Hydrolysis of Heptamethyl Methylmaltoside.—Method A. In studying this reaction the preparations of the alkylated maltoside obtained from different specimens of maltose were kept apart and treated separately; identical results were, however, obtained in each case.

The maltoside was hydrolysed by heating with 5% aqueous hydrochloric acid as described by Haworth and Leitch, but a variation was introduced into the method of separating the sugars, the acid liquor being extracted six times with chloroform. The syrup isolated from the chloroform solution crystallised at once and consisted of tetramethyl glucose.

The sugar remaining in the aqueous liquor was recovered in the usual manner and converted into the corresponding methylglucoside by boiling with methyl alcohol containing 1% of hydrogen chloride until the solution was devoid of reducing action. After rendering alkaline by the addition of sodium bicarbonate, the alcohol was removed and the residue taken up in water. On extracting six times with chloroform, the trimethyl methylglucoside passed into solution in the chloroform, from which it was recovered and purified by distillation at 145°/0·6 mm. This treatment removed traces of impurity and the glucoside was then rehydrolysed with 5% aqueous hydrochloric acid. On isolation of the product in the usual manner, the trimethyl glucose was obtained as a viscous syrup which slowly crystallised in the manner characteristic of 2 : 3 : 6-trimethyl glucose. The sugar was recrystallised from ether and identified as afterwards described.

In order to secure control evidence, the above operations were conducted in lots of 10 g., a typical result being that 10·3 g. of heptamethyl methylmaltoside gave 4·7 g. of crystalline tetramethyl glucose and 4·7 g. of syrupy trimethyl glucose. The latter, in turn, yielded 3·6 g. of distilled trimethyl methylglucoside, from which 3·3 g. of the corresponding sugar were obtained.

Method B. The hydrolysis of heptamethyl methylmaltoside was in this case conducted under conditions which would convert the liberated sugars into the corresponding methylglucosides. This was effected by boiling with excess of methyl alcohol containing 1% of hydrogen chloride, it being found that, in the course of 7 hours' treatment, the specific rotation, which had gradually diminished, attained a constant value. Boiling was continued for an additional period of 5 hours, after which the acid was neutralised and the solvent alcohol removed. The residue was then dissolved in water and the solution extracted repeatedly with chloroform, a syrup being obtained on evaporating the latter solvent. This syrup was a mixture of tetramethyl and trimethyl methylglucosides which was purified from traces of extraneous products by distillation under diminished pressure. The total distillate was thereafter hydrolysed in the usual manner by means of aqueous hydrochloric acid and the two sugars thus formed were separated by extraction with chloroform as described in Method A. The results were as before, crystal-

line tetramethyl glucose being isolated from the chloroform solution and the aqueous liquor retaining trimethyl glucose. This was isolated initially as a syrup which crystallised on keeping. In this particular instance, the solidification of the sugar was complete only after an interval of 3 weeks owing, it would appear, to the presence of a small proportion of a very viscous syrup which was less soluble in ether and had a smaller methoxyl content than trimethyl glucose. The crystallisation of the sugar was delayed by cooling and proceeded more satisfactorily at room temperature.

Examination of the Hydrolysis Sugars.—Identification of 2 : 3 : 4 : 6-*tetramethyl glucose.* The identification of the tetramethyl glucose presented no difficulty. All the specimens were recrystallised three times from light petroleum. The composition, melting point, mixed melting point, and mutarotation determined on the product agreed exactly with the accepted standards for 2 : 3 : 4 : 6-tetramethyl glucose.

Identification of 2 : 3 : 6-*trimethyl glucose.* In the hydrolysis experiments already described, the trimethyl glucose was obtained as a crystalline mass which still retained a small quantity of a viscous syrup. The material was thoroughly incorporated with dry ether containing a little acetone, and the crop of crystals removed by filtration. On evaporation of the filtrate and extraction of the residue with ether any non-crystallisable syrup was left undissolved, while the extract gave further crops of crystalline sugar. In one instance, when the proportion of adhering syrup was larger than usual, it was removed by draining on porcelain, from which it was recovered and examined, with negative results, for 2 : 3 : 4-trimethyl glucose. Each preparation of the sugar was purified by recrystallisation from ether containing a small proportion of low-boiling petroleum. In this way, the compound was obtained in characteristic long needles melting at 113—114° and showing no depression of the melting point when mixed with a standard specimen of 2 : 3 : 6-trimethyl glucose (Found: OMe, 41·2. Calc., 41·9%). When dissolved in water the sugar displayed downward mutarotation, giving the equilibrium value $[\alpha]_D^{20°}$ + 70·9°, the accepted permanent specific rotation for 2 : 3 : 6-trimethyl glucose being +70·5°. The results quoted are typical of those obtained with all the specimens examined.

Preparation of Methylmaltoside.—In order to attain greater accuracy, the reactions of methylation and hydrolysis were duplicated using crystalline methylmaltoside as the starting material. As a number of interesting features were encountered in the preparation of methylmaltoside, these are referred to now, together with such practical details as we have found to be advantageous.

Stage I. The preparation of octa-acetyl maltose proceeds most satisfactorily when not more than 30 g. of maltose are used in each experiment. In successive preparations 300 g. of the sugar were converted into the acetate, each experiment yielding on an average 20 g. of product which had been recrystallised from alcohol until the m. p. was 158—159°.

Stage II. Trial experiments showed that the action of hydrogen bromide on octa-acetyl maltose gives the best results when carried out on small quantities of the order of 2 g. This may be increased to a maximum of 10 g. but, with larger quantities, degradation of the disaccharide takes place and serious difficulties are introduced into the purification of the acetylated methyl-maltoside. By tedious repetition of the typical experiment now described, 250 g. of the octa-acetate were converted into hepta-acetyl methylmaltoside. 2 G. of octa-acetyl maltose were dissolved in 50 c.c. of a mixture consisting of glacial acetic acid saturated with hydrogen bromide (10%), of ether (15%), and of benzene (75%). The use of this particular mixture of solvents secures a permanently clear solution which enables the reaction to be followed by reliable polarimetric readings. The rotation of the solution came to a constant value in about 12 hours, the final specific rotation, recalculated for the change of concentration, ranging between + 184° and + 190°. The solution was washed twice with water and dried over anhydrous sodium sulphate, the solvent being thereafter removed. The residual syrup was dried in a vacuum at a temperature not exceeding 55°, a process which was accompanied by vigorous frothing.

Stage III. The bromo-derivative was dissolved by shaking with anhydrous methyl alcohol in the presence of silver carbonate, mixing being conducted on a mechanical shaker until a test sample of the solution was free from bromine. At this stage crystals of the product usually separated and consequently both the silver residues and the filtrate were extracted with hot chloroform. On removal of the solvent, hepta-acetyl methylmaltoside remained as a syrup which crystallised readily and was purified from absolute alcohol. In the course of 10 parallel preparations it was found that, as a rule, three crystallisations from alcohol gave a product melting at 124—125°, but, by repeating the crystallisation, this value could be raised to 128—129° (Found: C, 49·8; H, 5·9; OMe, 4·5. Calc., C, 49·8; H, 5·8; OMe, 4·8%. $[\alpha]_D$ in chloroform + 53° for $c = 1·5$). This melting point is identical with that quoted by Koenigs and Knorr, who prepared the compound from the corresponding nitrate. The loss sustained in these recrystallisations is considerable, as only about 40% of the original material is obtained in the pure condition.

In addition, a second crystalline product was isolated in amounts which varied in different preparations and it may be noted that when this substance was present in large proportion it was impossible to separate it from hepta-acetyl methylmaltoside by ordinary fractional crystallisation. Normally, this by-product was deposited from the mother-liquors, accumulated in the course of recrystallising hepta-acetyl methylmaltoside, when kept in a cool place. After recrystallisation from alcohol the compound melted at 145—146°, and showed $[\alpha]_D$ in chloroform + 69·1° for $c = 1·5$ (Found: OMe, 5·2; $CH_3·CO_2H$, 63·3. Calc. for $C_{24}H_{34}O_{16}$, OMe, 5·4; $CH_3·CO_2H$, 62·3%). The examination in detail of this compound will form the subject of a later communication.

Stage IV. Hepta-acetyl methylmaltoside, in quantities of about 40 g., was dissolved in a large excess of absolute alcohol saturated with dry ammonia. After 2 days, the rotation of the solution became constant and thereafter the solvent was removed under diminished pressure. The viscous syrup then remaining was dissolved in the minimum amount of alcohol and the methylmaltoside precipitated by the addition of small quantities of a mixture of chloroform and ether. The product was thereafter repeatedly recrystallised from a mixture of alcohol and ethyl acetate—a process which, if wasteful, is necessary before the maximum melting point of 110—111° is attained. Average yield, 9·5 g. In this condition, methylmaltoside contained 1 molecule of combined water (Found: OMe, 8·3; H_2O, 4·9. Calc. for $C_{13}H_{24}O_{11},H_2O$, OMe, 8·3; H_2O, 4·8%).

The following observations were made on a specimen dried over phosphoric anhydride at 100°/15 mm.: C, 43·8; H, 7·0. Calc. for $C_{13}H_{24}O_{11}$, C, 43·8; H, 6·75%. $[\alpha]_D$ in alcohol + 63·5° for $c = 1$; in water, + 83·9° for $c = 1$.

Methylation of Methylmaltoside.—This methylation was carried out by the silver oxide reaction in a manner parallel with that employed in the case of methylglucoside. In the first three methylations it was necessary to use methyl alcohol as an extraneous solvent, but thereafter the material was freely soluble in methyl iodide alone. After the sixth methylation, the refractive index was 1·4689 and the methoxyl content 50·1%. Two additional methylations failed to alter n_D, although the methoxyl content had increased to 52·3%. On distillation in a high vacuum, no lower-boiling distillate was obtained and the material distilled sharply at the boiling point of heptamethyl methylmaltoside (Found: n_D, 1·4662; yield, 76%; C, 52·7; H, 8·45; OMe, 54·1. Calc. for $C_{20}H_{38}O_{11}$, C, 52·9; H, 8·4; OMe, 54·6%).

Solvent.	c.	$[\alpha]_D$.
Water	0·508	+88·1°
Alcohol	0·562	81·9
Chloroform	0·557	78·9
Acetone	0·577	78·1

Hydrolysis of Heptamethyl Methylmaltoside.—A 4·5% solution of the compound in 5% aqueous hydrochloric acid was boiled until the rotation, which at first diminished, increased to a constant value. Judging from the initial polarimetric reading, it would appear that hydrolysis commenced in the cold.

Time. ($l = 1$).	a.	$[\alpha]_D$.
Start	+3·11°	+69·3°
15 mins'. boiling	2·68	59·6
1 hour's „	2·85	63·4
2¾ „ „	3·27	72·3 constant.

After neutralising the solution with barium carbonate it was decolorised with norit and extracted six times with chloroform. The extract gave crystalline tetramethyl glucose (yield, 91% of the theoretical amount). Trimethyl glucose was recovered from the aqueous liquor by evaporation and extraction of the residue with acetone. Removal of this solvent left a syrup which was taken up in ether containing a trace of acetone and treated as already described. The trimethyl glucose crystallised rapidly, solidification beginning spontaneously in a few hours (yield, 87% of the theoretical amount).

Tetramethyl glucose. After two recrystallisations, m. p. 93—95°; $[\alpha]_D$ in absolute alcohol + 112·1° (initial) → 83·4° (constant).

Trimethyl glucose. After two recrystallisations, m. p. 113—114°; mixed m. p. 113—114°; permanent specific rotation in water + 70·2°; OMe, 41·6%. All the above determinations agree exactly with the standard values for 2 : 3 : 6-trimethyl glucose and further confirmation was obtained by converting the sugar into the corresponding β-methylglucoside. This proved to be identical with the trimethyl methylglucoside obtained from cellulose; m. p. 57·5°; mixed m. p. 57°; C, 50·6; H, 8·4; OMe, 51·9. Calc., C, 50·8; H, 8·5; OMe, 52·5%. The specific rotation in methyl alcohol for $c = 1$ was − 29·3°.

The thanks of the authors are due to the Carnegie Trust for a Research Fellowship held by one of them, and also to Dr. J. W. H. Oldham and to Mr. C. B. Purves (Carnegie Fellows) for much valuable help in carrying out control experiments.

United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, February 20th*, 1926.]

CXX.—*The Constitution of the Disaccharides. Part X. Maltose.**

By CONRAD J. ASTLEY COOPER, WALTER NORMAN HAWORTH, and STANLEY PEAT.

THE investigation of the structure of maltose by Haworth and Leitch (J., 1919, **115**, 809) was one of the earliest of those undertaken in the disaccharide series. In the interval which has elapsed, greater familiarity with the properties and mode of identification of the partly methylated glucoses, and particularly of the trimethyl glucoses, has been gained.

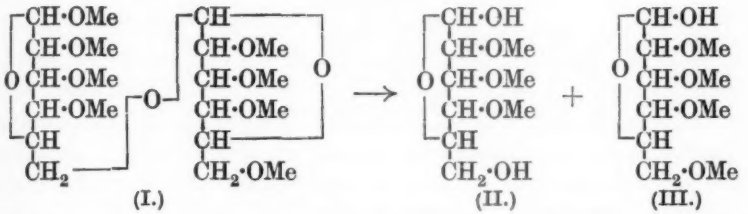
During a research, which will shortly be published, on the constitution of Ling and Nanji's *iso*maltose (J., 1923, **123**, 2666), certain irregularities were revealed which led us to suspect the accuracy of the formula previously applied to maltose. Consequently, the study of the latter sugar has been again undertaken during the past 18 months, with results which seem to require a modification of Fischer's formula for maltose, which was supported by the work of Haworth and Leitch.

In the earlier paper, the structural formula which appeared to represent maltose showed the linking of the two hexoses as occurring through the primary alcohol residue of one hexose with the reducing group of the second. The experimental data on which this conclusion was based were dependent on the recognition of the structure of the trimethyl glucose (II) obtained, along with tetramethyl glucose (III), by hydrolysis of heptamethyl methylmaltoside (I). In these formulæ the revised structure for normal glucose is used (Charlton, Haworth, and Peat, this vol., p. 89); consequently the older 2 : 3 : 5-trimethyl glucose is now written as 2 : 3 : 4-trimethyl glucose.

The facts available at that time pointed to the non-identity of this specimen of trimethyl glucose, which was a liquid, with crystalline 2 : 3 : 6-trimethyl glucose, which was isolated as a hydrolysis product of methylated cellobiose (Haworth and Hirst, J., 1921, **119**,

* Almost the whole of the experimental results given in this paper were obtained during the early part of 1925, but publication was held over for the inclusion of other confirmatory details. A private communication from Sir James Irvine was received on February 28th, 1926, intimating, but without experimental details, that he had communicated a paper to the Society announcing the isolation of 2 : 3 : 6-trimethyl glucose as a hydrolysis product of methylated maltose. In the circumstances, we consider it is advisable now to submit our results for publication, inasmuch as they may serve to confirm and supplement those obtained by Irvine and his collaborators, whose priority we acknowledge.

193). Moreover, the oxidation of the trimethyl glucose derived from methylated maltose led to the isolation of what was considered to be a trimethyl saccharolactone (IV), and for these reasons, since the primary alcohol residue had apparently undergone oxidation to a carboxyl group without loss of a methoxyl residue, the specimen of trimethyl glucose was considered to have three methoxyl residues in the 2 : 3 : 4-positions, as shown in formula (III).



(I.) (II.) (III.)

In a new series of experiments, the whole of the early work was repeated, and gave identical analytical results for the oxidation product of the trimethyl glucose. The method of isolating the trimethyl glucose was then modified, and instead of separating the hydrolysis products of methylated maltose by distillation, the aqueous solution containing the methylated hexoses was repeatedly extracted with chloroform, which entirely removed tetramethyl glucose as the normal crystalline variety (2 : 3 : 4 : 6).

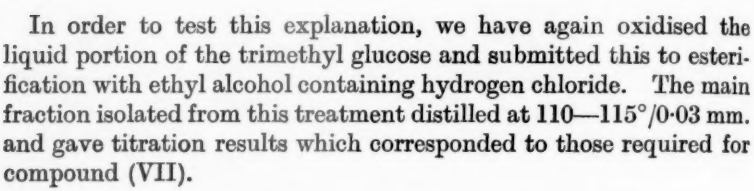
Remaining in the aqueous solution was the trimethyl glucose, and this was recovered by evaporation followed by extraction. The extracted syrup spontaneously crystallised, and yielded about 6% of the total in the form of the readily identifiable 2 : 3 : 6-trimethyl glucose. This was similar in all respects to the specimen previously isolated both from methylated cellobiose and from methylated lactose. Moreover, the remaining syrup appeared to consist of the β-form of this normal sugar, and probably contained also α- and β-forms of the corresponding γ-sugar, into which the normal variety appears to pass somewhat readily owing to the presence of a free hydroxyl group in the γ-position in the chain. Possibly owing to the latter consideration, crystalline 2 : 3 : 6-trimethyl glucose cannot be isolated in quantity.

An alternative interpretation to that given in the earlier paper by Haworth and Leitch can now be offered, inasmuch as, accepting the trimethyl glucose as in reality 2 : 3 : 6-trimethyl glucose (V), this could pass on oxidation to dimethyl saccharolactone (VI). Under the experimental conditions described by Haworth and Leitch, the oxidation product from the trimethyl sugar was digested with ethyl alcohol for the purpose of removing traces of water, and it would appear to have undergone partial transformation

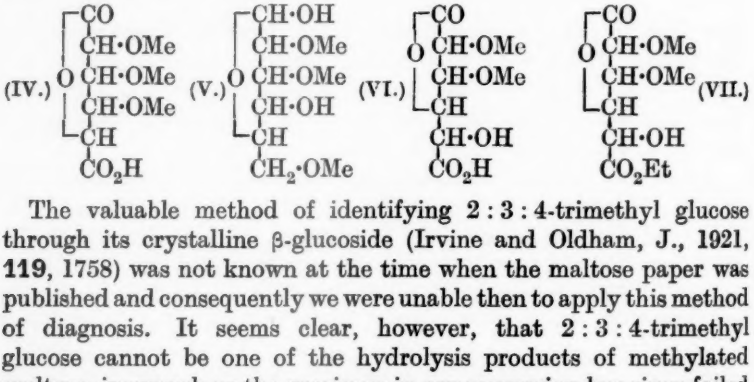
into the ethyl ester of the dimethyl saccharolactone. The analytical data previously quoted are given in column 1, and those of dimethyl saccharolactone (VI) and its ethyl ester (VII) in columns 2 and 3. The mean of the latter two results, given in column 4, will be seen to be closely similar to the analytical data previously interpreted under column 1 as indicating the constitution of the product as that of a trimethyl saccharolactone.

	1.	2.	3.	4.
C	46·03	43·6	48·4	46·0
H	6·26	5·45	6·46	5·95
OMe	35·9	28·2	37·5	32·85

In order to test this explanation, we have again oxidised the liquid portion of the trimethyl glucose and submitted this to esterification with ethyl alcohol containing hydrogen chloride. The main fraction isolated from this treatment distilled at 110—115°/0·03 mm. and gave titration results which corresponded to those required for compound (VII).



The valuable method of identifying 2 : 3 : 4-trimethyl glucose through its crystalline β-glucoside (Irvine and Oldham, J., 1921, **119**, 1758) was not known at the time when the maltose paper was published and consequently we were unable then to apply this method of diagnosis. It seems clear, however, that 2 : 3 : 4-trimethyl glucose cannot be one of the hydrolysis products of methylated maltose, inasmuch as the specimen in our possession has since failed to satisfy those tests. The β-glucoside, when prepared, did not crystallise on keeping or on nucleation with specimens of 2 : 3 : 4-trimethyl β-methylglucoside which had been isolated for purposes of



diagnosis during our work on the constitution of gentiobiose and of amygdalin biose. On the other hand, the isolation of crystalline

2 : 3 : 6-trimethyl glucose points to the necessity of revising the structural formula of maltose, to which is now given the constitution (VIII) or (IX). The formula (VIII) differs stereochemically but not structurally from that of cellobiose, since the latter is a glucose β-glucoside and maltose is a glucose α-glucoside.

The adjustment of the formula of maltose removes many outstanding anomalies as to the behaviour of starch.

Experimental.

Hydrolysis of Heptamethyl Methylmaltoside. Isolation of 2 : 3 : 6-Trimethyl Glucose and 2 : 3 : 4 : 6-Tetramethyl Glucose.—A specimen of heptamethyl methylmaltoside (39·5 g.) prepared as previously described by Haworth and Leitch (*loc. cit.*) (b. p. 201—203°/0·03 mm.) was hydrolysed by digesting with 5% hydrochloric acid at 85° for 1½ hours and at 100° for a further period of 1½ hours. Thereafter the specific rotation of the solution remained constant, and the hydrolysis was complete. The neutralised solution was slightly concentrated under diminished pressure and extracted several times with large quantities of chloroform. The chloroform extract was dried and evaporated; the residual syrup crystallised almost immediately, yielding pure 2 : 3 : 4 : 6-tetramethyl glucose (16·5 g.).

The residual aqueous solution was completely evaporated under diminished pressure and gave a syrup (15 g.) which, on keeping for several weeks, partly crystallised. These crystals (m. p. 106—117°) were drained on porous tile, and purified by solution in dry ether, from which small, colourless needles separated in three fractions: (a) m. p. 105—111°; (b) 108—115°; (c) 102—109°. Further recrystallisation gave crystals (1·25 g.), m. p. 110—116°, which, in admixture with a specimen of 2 : 3 : 6-trimethyl glucose derived from methylated lactose (Haworth and Leitch), showed no depression of melting point. It showed in methyl alcohol ($c = 1·73$) $[\alpha]_D$ +102·6° after 15 minutes, changing to 70·2° after 12 hours, and, after catalysis, to 67·5° (Found: C, 48·4; H, 8·3; OMe, 40·4. Calc., C, 48·6; H, 8·1; OMe, 41·9%).

The uncrystallisable syrup from which the above crystals had been obtained was oxidised by digestion with nitric acid (d 1·2), heating to 80° until brown fumes began to be evolved, and thereafter at 70° for 5½ hours. After being cooled and tested for the presence of free sugar, the solution was again heated for a short period until the whole of the sugar was oxidised. The nitric acid was then removed by distillation under diminished pressure at 35°, water being constantly added during this operation. Finally, the whole of the water was evaporated, and the syrupy residue dissolved in ethyl alcohol containing 2% of hydrogen chloride. This solution

was boiled for 8 hours in order to complete the esterification, and the product was isolated in the usual manner. The methoxyl and ester groups were determined by the Zeisel method, calculating both OMe and OEt in terms of OMe, and showed 40·6%. The ester was then distilled, the first portion being collected at 88—95°/0·03 mm., but the main portion, the analysis of which is given below, distilled at 110—115°/0·03 mm. (Found: OR, 39·3. Calc. for the ethyl ester of dimethyl saccharolactone, $C_{10}H_{16}O_7$, 37·5%).

Titration. 0·1108 G. required 4·7 c.c. of *N*/10-sodium hydroxide in the cold, and on heating in a water-bath with excess of the alkali for 20 minutes, a total of 8·81 c.c. of *N*/10-sodium hydroxide was required. Calculated for the ethyl ester of dimethyl saccharolactone, $C_{10}H_{16}O_7$, 8·92 c.c., and for the trimethyl saccharolactone, $C_9H_{14}O_7$, 9·46 c.c. Hydrolysis of this ester gave dimethyl saccharolactone (Found: OMe, 27·8. Calc.: OMe, 28·2%).

On another occasion, the whole of the work described in the paper by Haworth and Leitch (*loc. cit.*) on the constitution of maltose was repeated in every detail, and the lactone derived from the oxidation of trimethyl glucose was titrated and gave the following results: 0·0979 g. required 8·37 c.c. of *N*/10-sodium hydroxide. Calculated for trimethyl saccharolactone, $C_9H_{14}O_7$, 8·33 c.c. In the earlier paper, a small typographical error appeared in the account given of the titration results, and the above re-determination was therefore carried out. This anomaly is explained in the introduction.

The authors express their thanks to the Department of Scientific and Industrial Research for the award of a grant to one of them.

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CXXI.—*Synthesis of Derivatives of γ-Xylose.*

By WALTER NORMAN HAWORTH and GEORGE CRONE WESTGARTH.

THIS investigation forms a part of a general study of the constitution of the normal and the γ-forms of the sugars. The isolation of derivatives of γ-fructose, γ-galactose, and γ-arabinose encouraged the view that the existence of γ-forms was a general property of the sugars (Haworth and Law, J., 1916, **109**, 1314; Haworth, Ruell, and Westgarth, J., 1924, **125**, 2468; Baker and Haworth, J., 1925, **127**, 365).

In the present paper, another example in the pentose series is

described, namely, *trimethyl γ-xylose*, the structure of which has been investigated by conversion into its lactone and comparison of the properties of the latter with the corresponding lactone which we have isolated from normal trimethyl xylose.

In the case of xylose, the condensation with methyl alcohol in the cold proceeds very tardily, the *γ-methylxyloside* requiring 5 to 7 days for its formation, as contrasted with fructose, which condenses with methyl alcohol in the course of ½ hour, and galactose and arabinose, which require a period of less than a day after solution of the sugar. In following the formation of the γ-methylxyloside polarimetrically, it was observed that the condensation was accompanied by no inversion in the sign of rotation, and indeed, the final value recorded, $[\alpha]_D$ + 28·8°, differed very little from the initial value, + 28·3°, of the original xylose solution, although intermediate readings attained a maximum of + 37·7°.

γ-Methylxyloside is comparable in its properties with γ-glucosides in general, exhibiting the usual ease of hydrolysis with acids of extreme dilution, and the characteristic instability in presence of neutral permanganate. From the specimen of γ-methylxyloside, the completely methylated derivative, *trimethyl γ-methylxyloside*, was obtained as a colourless liquid, $[\alpha]_D$ = + 32·0° in methyl alcohol. Hydrolysis of this compound was effected at 100° with either *N*/50- or *N*/100-hydrochloric acid, but for the purpose of the preparation of the corresponding free sugar *N*/15-acid may conveniently be used, the hydrolysis being complete in 4 hours. The rotation changes accompanying the hydrolysis exhibited the usual fall and rise in value, giving a time-period curve characteristic of the γ-glucosides, and indicating the presence of two stereochemical forms.

Trimethyl γ-xylose was thus isolated as a liquid containing both α- and β-forms, and its properties were compared with those of the normal trimethyl xylose prepared by Carruthers and Hirst (J., 1922, **121**, 2306).

	Trimethyl γ-xylose.	Normal trimethyl xylose.
	Syrup, b. p. 110°/0·04 mm.	Crystalline, m. p. 87—90°.
$[\alpha]_D$	+24·7° ⟶ 31·2°.	+74° ⟶ 21°.
Action of permanganate.	Reduces vigorously.	No action.
Acid methyl alcohol.	Combines rapidly.	Combination slow.

It is noteworthy that these two structurally different forms should display specific rotations of the same sign and of similar magnitude. In this respect, the two varieties of trimethyl xylose may be compared with those of tetramethyl mannose, the γ-form

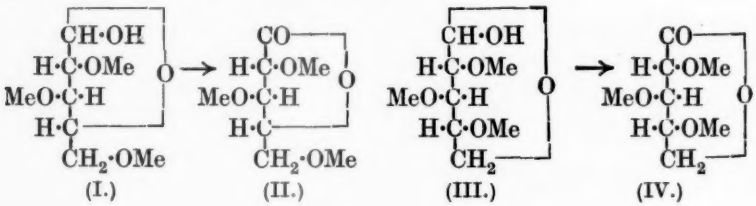
of which is crystalline and shows $[\alpha]_D + 48{\cdot}5°$, whereas the normal form is a liquid, showing $[\alpha]_D + 17{\cdot}2°$ (equilibrium in methyl alcohol) (Irvine and Burt, J., 1924, **125**, 1343).

With the object of deriving the constitution of trimethyl γ-xylose, the sugar was oxidised to the corresponding *lactone*, and for the purposes of comparison a similar procedure was followed also with the normal sugar. The properties of the two lactones are indicated below :

Lactone from	(*a*) Trimethyl γ-xylose. Liquid.	(*b*) Normal trimethyl xylose. Crystalline, m. p. 55°.
$[\alpha]_D$ in water.	$+74{\cdot}1° \longrightarrow 61{\cdot}4°$ (Period, 21 days).	$-3{\cdot}8° \longrightarrow +20{\cdot}8°$ (Period, 8 days).

A comparison of these rotation values indicates that the lactone from the γ-sugar resists hydrolysis to a much greater extent than the corresponding lactone from the normal sugar, and curves representing these changes have been given in the paper by Charlton, Haworth, and Peat (this vol., p. 93).

Since the constitution (III) allocated to normal trimethyl xylose on the basis of its oxidation to trimethoxyglutaric acid is that of a normal or δ-oxide (Hirst and Purves, J., 1923, **123**, 1352), it is evident that the structure of the derived lactone is that indicated by formula (IV). We are able to assign the structural formula (II) to the lactone from the γ-sugar for two reasons : (*a*) Its lactone ring must be situated on the right of the carbon chain on the basis of Hudson's rule, since the substance displays dextrorotation, diminishing in magnitude as the ring opens by hydrolysis to the hydroxy-acid. The lactone ring cannot engage the β-carbon acid, since in this case the lactone would be lævorotatory. (*b*) Its speed of hydrolysis in water is comparable in every respect with the series of γ-lactones examined by Charlton, Haworth, and Peat (*loc. cit.*). We therefore ascribe the constitution of a γ-lactone to this compound (II), whence it follows that the related sugar, trimethyl γ-xylose, has the constitution (I).



EXPERIMENTAL.

Preparation of γ-Methylxyloside.—Polarimetric observations indicated that at 15° solutions of xylose (2%, 3·5%, and 5%) in dry,

acetone-free methyl alcohol containing 1% of hydrogen chloride attained a maximum rotation after 25—30 minutes from the time of solution, this stage being succeeded by a slow diminution of rotation, and the equilibrium period seemed to be reached in about 24 hours.

The following values were obtained, for example, with a solution of this nature containing 2% of xylose :

Time (mins.)	5	10	15	20	30	53	58
$[\alpha]_D$	+28·3°	35·3°	37·2°	37·4°	37·7°	36·1°	35·9°
Time (mins.)	163	210	22½ hrs.				
$[\alpha]_D$	+30·9°	29·0°	28·8°				

With a similar solution containing, however, 5% of xylose, the following polarimetric figures were recorded :

Time (mins.)	20	26	36	52	62	72	112
$[\alpha]_D$	+37·9°	38·6°	38·8°	38·5°	37·5°	37·0°	35·3°
Time (mins.)	167	262	397				
$[\alpha]_D$	+33·5°	32·1°	30·3°				
Time (hours)	25	50	75				
$[\alpha]_D$	+29·3°	28·5°	28·2°	(Thereafter, apparently constant.)			

The evidence furnished by tests with Fehling's solution, and also by actual isolation of the product, indicated that xyloside formation was far from complete at the end of these periods.

It thus appeared that glucoside formation proceeded very slowly under these conditions, xylose differing markedly in this respect from fructose, galactose, and arabinose. Moreover, the apparent attainment of a constant rotation after 24 hours was deceptive, in that methylxyloside continued to be formed even after 5 days, although the rotation changes were negligible during this extended period.

The following experimental conditions were therefore adopted for the preparation of larger quantities of γ-methylxyloside : Dried, finely-sieved xylose (11·9 g.) was dissolved in 238 g. of pure dry methyl alcohol containing 2·27 g. of hydrogen chloride, making a 5% solution of xylose in methyl alcohol containing 1% of hydrochloric acid. The mixture was kept at room temperature until it no longer reduced Fehling's solution, this stage being reached after 7 days. The product, isolated in the usual manner, was extracted with ethyl acetate, and consisted of a viscid syrup (8 g.) containing 0·7 g. of xylose crystals, which were removed by solution of the syrup in absolute alcohol. Distillation of the syrup was effected without any decomposition, giving rise to a pale yellow, viscid product, b. p. 161·5°/0·03 mm., $[\alpha]_D = +62·8°$ in ethyl alcohol [Found : OMe, 18·4. $C_5H_9O_4(OMe)$ requires OMe, 18·8%].

In another preparation of γ-methylxyloside, 27·5 g. of xylose

gave 20·6 g. of a syrup from which 15·8 g. of the distillate were obtained, the still residue being 3·4 g. In this experiment, the solution ceased to reduce Fehling's solution after 5 days.

Methylation of γ-Methylxyloside.—Methylation of this product was carried out with methyl sulphate and sodium hydroxide, care being taken to prevent development of acidity during the operation. The first eighth of each reagent was added at 40°, the second at 55°, and the remainder at the usual temperature of 70°. The quantities used were : γ-methylxyloside, 6·3 g.; methyl sulphate, 16·3 c.c.; sodium hydroxide, 15·5 g. in 31 c.c. of water. This yielded a pale liquid product which was remethylated with methyl iodide and silver oxide. The liquid product weighed 3·5 g. and had b. p. 78°/0·03 mm., $n_D = 1·4407$. A small quantity of crystals was also collected.

The distilled liquid was colourless and immediately reduced neutral permanganate in the cold, but showed no reduction of Fehling's solution even on vigorous boiling [Found : C, 51·35; H, 8·4; OMe, 56·3. $C_5H_6O(OMe)_4$ requires C, 52·4; H, 8·7; OMe, 60·2%. $C_5H_7O_2(OMe)_3$ requires C, 50·0; H, 8·3; OMe, 48·3%].

These figures indicated that the xylose compound contained between three and four methoxyl groups.

The material was mixed with a further 11·2 g. which had been methylated to the same stage, and the whole (14·4 g.) was remethylated six times by Purdie's reagents. On distillation the first few drops were rejected, and a yield of 10·05 g. of the main fraction, b. p. 82·5—84·5°/0·03 mm., was obtained. In order to ensure a better fractionation, this product was re-distilled in the vacuum of the water-pump and then had b. p. 110—114°/14 mm. (Found : C, 52·2; H, 8·8; OMe, 59·0. $C_9H_{18}O_5$ requires C, 52·4; H, 8·7; OMe, 60·2%). $[\alpha]_D = +32·0°$ in methyl alcohol ($c = 0·7975$); n_D 1·4387.

The sugar derivative was therefore a fully-methylated pentoside, and was essentially trimethyl γ-methylxyloside.

Preliminary Hydrolysis.—Preliminary experiments were instituted with the view of determining the ease of hydrolysis of trimethyl γ-methylxyloside with acid of varying dilutions. For this purpose hydrochloric acid (*a*) *N*/100; (*b*) *N*/50; (*c*) *N*/15 was employed at 100° and the following polarimetric data were recorded :

(*a*)	Time (mins.) ...	5	25	55	85	120	150	210	275
	$[\alpha]_D$	+37·9°	17·2°	16·3°	19·7°	22·0°	24·1°	28·6°	33·2°
(*b*)	Time (mins.) ...	3	27	57	89	109			
	$[\alpha]_D$	+33·9°	18·2°	24·2°	24·2°	26·4°			
(*c*)	Time (mins.) ...	0	30	60	150	240	360		
	$[\alpha]_D$	+35·6°	28·8°	34·2°	36·9°	38·3°	37·8°		

To the solution (*c*) sufficient concentrated hydrochloric acid was added to increase the *N*/15-acid to 1% strength, and this solution was kept at 100° for an hour, after which the specific rotation diminished from + 37·8° to 35·1°. By increasing the acid concentration to 5% and boiling the solution for a further period of 1½ hours the rotation fell to +29·9°. It was evident, therefore, that if any of the normal form of trimethyl methylxyloside was present in the original product, this quantity was extremely small, since normal trimethyl xylose has a lower specific rotation ($[\alpha]_D$+21°) and is formed from its glucoside by hydrolysis with 5% hydrochloric acid at 100°.

Isolation of Trimethyl γ-Xylose.—Trimethyl γ-methylxyloside (4·5 g.) was dissolved in 100 c.c of *N*/15-hydrochloric acid and heated under reflux on a boiling-water bath as in the above control experiment. The hydrolysis was arrested after 5 hours, when a constant rotation was reached. The solution was then neutralised with barium carbonate, filtered, and evaporated at 40°/12 mm. to a syrup. This was dissolved in chloroform, filtered from inorganic salt and evaporated, and the residual product (3·8 g.) was distilled.

Fraction 1. B. p. 96·5°/0·06 mm., 1·3 g., n_D = 1·4509.
„ 2. B. p. 110°/0·04 mm., 2·3 g., n_D = 1·4539.

The first fraction contained some unchanged xyloside, and any of the normal form of trimethyl methylxyloside which might be present would be collected in this fraction of lower boiling point since it would be unaffected by the *N*/15-acid.

The second fraction, consisting of trimethyl γ-xylose (Found: C, 49·5; H, 8·5; OMe, 47·2. $C_8H_{16}O_5$ requires C, 50·0; H, 8·3; OMe, 48·4%), was a colourless liquid which reduced Fehling's solution very actively, and also neutral permanganate in the cold. $[\alpha]_D$ in water, + 24·7° ⟶ 29·5° after 40 hours. After catalysis, the final equilibrium value was + 31·2°.

Oxidation of Trimethyl γ-Xylose with Bromine Water. Isolation of Trimethyl γ-Xylonolactone.—Trimethyl γ-xylose (1·5 g.) was dissolved in 12 c.c. of water, and 1 c.c. of bromine added gradually with shaking. The solution was then heated for 6½ hours at 30—35°. After keeping in the cold for 60 hours, it slightly reduced Fehling's solution. A further ½ c.c. of bromine was accordingly added and the oxidation completed by again heating for 9 hours at 35—40° and keeping over-night at room temperature. Excess of bromine was then removed by aeration, and the solution concentrated under diminished pressure. Hydrobromic acid was removed by the usual treatment, and the solution evaporated at 40°. The residual syrup was dissolved in dry ether and filtered several times

to remove traces of inorganic matter. In this way, 1·3 g. of a pale yellow liquid were obtained, which was submitted to fractionation in a high vacuum. Nearly the whole distilled at about 105°/0·04 mm., and showed n_D 1·4465 (Found: C, 50·7; H, 7·6; OMe, 47·4. Calc. for $C_8H_{14}O_5$, C, 50·5; H, 7·4; OMe, 48·9%).

On titration, the compound behaved as a lactone: 0·1060 g. required, on heating, 5·4 c.c. of *N*/10-sodium hydroxide (Calc. for $C_8H_{14}O_5$, 5·6 c.c.). The compound behaved in aqueous solution as a typical γ-lactone; there was a slow change in the value of the specific rotation due to the opening of the lactone ring, with formation of an acid of lower rotatory power. The following rotations were observed in aqueous solution ($c = 1·1062$): $[\alpha]_D$ + 74·1° after 5 minutes, 71·8° after 64 hours, 69·6° after 7 days, 61·4° after 21 days.

The experimental evidence stated above has led to the conclusion that the oxidation product was trimethoxy-γ-xylonolactone, and a 1 : 4 or butylene-oxide structure has thus been assigned to the derivatives of γ-xylose.

Preparation of Trimethyl δ-Xylonolactone from the Normal Form of Trimethyl Methylxyloside.—A simultaneous hydrolysis and oxidation of crystalline trimethyl β-methylxyloside (m. p. 48—49°) was carried out as follows (compare Pryde, Hirst, and Humphries, J., 1925, **127**, 348): A solution of the normal form of the xyloside (1·5 g.) in 16·6 c.c. of 3% aqueous hydrobromic acid was heated at 85° for an hour and cooled to 75°. Bromine was then added (0·7 c.c.) over a period of 4 hours at the rate of 7 drops every half-hour. The solution stood at room temperature for 24 hours and then a further 1 c.c. of bromine was added at 75° over a period of 4 hours at the rate of 10 drops every half-hour. The liquid still reduced Fehling's solution after cooling and keeping over-night. More bromine (0·5 c.c.) was introduced over a period of 6 hours at the same temperature as before. On keeping over-night, the oxidation was found to be complete, and the product was isolated in the usual way. The yellow liquid thus obtained (1·13 g.) crystallised on the addition of ether. It was considered advisable, however, to distil the product in order to decompose any free acid that might be present. The product having been heated on a bath at 100—110°/0·05 mm. for 1¼ hours, the bath temperature was raised to 145—150°; the product then distilled smoothly at 115—120°/0·05 mm. as a colourless liquid which solidified, and the crystalline mass was drained on porous tile (m. p. 52—53°). It recrystallised from light petroleum (sparingly soluble) in very long needles melting sharply at 55°. A further recrystallisation produced no change in the melting point. The recrystallised material resembled glass wool in appearance,

and analysis proved it to be trimethoxyxylonolactone, which must be the δ-lactone, since the normal trimethyl xylose gives rise on oxidation to trimethoxyglutaric acid (Hirst and Purves, *loc. cit.*) (Found : C, 50·8; H, 7·5; OMe, 48·9. Calc. for $C_8H_{14}O_5$, C, 50·5; H, 7·4; OMe, 48·9%). On titration the compound behaved as a lactone : 0·1025 g. required, on heating, 5·15 c.c. of *N*/10-sodium hydroxide (Calc. for $C_8H_{14}O_5$, 5·39 c.c.). The hydrolysis of the lactone in aqueous solution at room temperature ($c = 1·3289$) was followed polarimetrically : $[\alpha]_D^{15°}$ −3·8° after 4 minutes, + 2·3° after 1½ hours, + 3·0° 4 hrs., + 6·9° 23 hrs., + 15·8° 4 days, + 19·5° 6 days, + 20·8° 8 days.

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CXXII.—*Termolecular Reactions. Reduction of Silver Acetate by Sodium Formate.*

By ALEXANDER COUTIE.

IN a recent investigation of the reaction occurring between formaldehyde and bases, the author had occasion to make use of various velocity equations, in an attempt to settle the order of reaction. A comparison of the formulæ employed by other experimenters, working along similar lines, showed that in many cases these were in error. This can best be explained by reference to the fundamental differential equation, which is readily arrived at in the following way.

Multimolecular chemical reactions are of two types. The first class consists of those in which the participation of one molecule of each of n different substances, all originally of the same molar concentration, is necessary and sufficient for the occurrence of the change. The differential equation assumes the form

$$-dC/dt = kC^n \qquad (1)$$

(All concentrations in this section may be taken as measured in g.-mols. per litre.) The other class is much more general, and includes those reactions in which the n molecules, taking part in the change, are not all different. If m_1 molecules of substance A,

reacting with initial concentration C_1, disappear for every m_2 molecules of substance B—of original concentration C_2—and so on

$$-dC/dt = kC_1^{m_1}C_2^{m_2}C_3^{m_3} \ . \ . \ . \qquad (2)$$

where $m_1 + m_2 + m_3 + \ . \ . \ . \ = n$.

This equation can be put in a more useful form. If several substances A, B, C, . . ., with initial concentrations a, b, c, . . ., take part in a simple reaction, undisturbed by any simultaneous or secondary changes, and if l, m, n, . . . are the numbers of molecules of A, B, C, . . . which must react simultaneously before the change considered can take place, then, when x is the actual fall in concentration, in time t, of a substance of which only one molecule is necessary for the progress of the reaction,

$$dx/dt = k(a - lx)^l\,(b - mx)^m(c - nx)^n \ . \ . \qquad (3)$$

the number of factors being equal to the number of different substances taking part in the reaction. A similar equation has been given by Wegscheider (*Z. physikal. Chem.*, 1900, **35**, 513).

From this general equation can be deduced all the ordinary unimolecular, bimolecular, etc., velocity formulæ, but in certain cases it leads to forms at variance with those already mentioned as being employed by a number of investigators. The disputed equations refer to reactions in which two or more molecules of at least one of the substances present are necessary for the progress of the change, *i.e.*, when one or more of the quantities l, m, n, . . . in equation (3) is greater than unity. Applied to termolecular reactions of this type, as being those with which the author was chiefly concerned, the general equation gives the following formulæ.

Termolecular.—When a change takes place involving the interaction of three molecules of A, the sole reactant present, equation (3) reduces to

$$dx/dt = k(a - 3x)^3 \qquad (4)$$

but when two molecular species A and B take part—their initial concentrations being a and b, respectively—and two molecules of B react with one of A, then

$$dx/dt = k(a - x)(b - 2x)^2 \qquad (5)$$

In a formula such as (4)—where a is the total initial concentration of the reactant of which three molecules take part in the change, and x is the reduction in concentration, in time t, due to *each* molecule reacting—it is quite allowable, if absolute values of the velocity coefficient are not required, to make the substitution $x_1 = 3x$, whence

$$dx_1/dt = k_1(a - x_1)^3 \qquad (6)$$

and $k_1 = 3k$. It is obviously not justifiable to make such a substitution in one term of a differential equation and not in another. For example, the values of k obtained from equation (5) are not constant multiples of those derived from the form

$$dx/dt = k(a - x)(b - x)^2 \qquad (7)$$

It is in this virtual neglect of the coefficients of x that the experimenters already referred to were in error.

For instance, Noyes and Cottle (*Z. physikal. Chem.*, 1898, **27**, 579; *J. Amer. Chem. Soc.*, 1899, **21**, 250) employ formula (7) in their study of the reaction between silver acetate and sodium formate, which may be represented by the equation

$$2CH_3{\cdot}CO_2Ag + H{\cdot}CO_2Na = 2Ag + CO_2 + CH_3{\cdot}CO_2H + CH_3{\cdot}CO_2Na.$$

They state that in this formula a and b are the initial concentrations of sodium formate and silver acetate, respectively, and x the measured fall in concentration of the latter substance. Although the concentration of the silver acetate falls at twice the rate of that of the sodium formate, their formula does not show this. Moreover, their formula is restricted in its application when a is less than b, in which case it can only be employed as long as x is less than a, *i.e.*, during the first half of an experiment. Noyes and Cottle continued their work past the point of half-decomposition in all experiments except, unfortunately, those to which this applies. The formula which they should have used is evidently

$$dx/dt = k(a - x/2)(b - x)^2 \qquad (8)$$

This is identical in form with equation (5).

The use of erroneous formulæ of the above type by several workers is possibly due to their having accepted without question or appropriate modification those given by Ostwald ("Lehrbuch der allgemeinen Chemie," 1887, II, 615—634) and integrated by Fuhrmann (*Z. physikal. Chem.*, 1889, **4**, 89), which are all of a simple and straightforward nature.

Reduction of Silver Acetate by Sodium Formate.

Since the days of van 't Hoff it has been recognised that reactions of order higher than the second are few in number, and certain examples brought forward from time to time have been severely criticised and shown to afford little or no evidence in favour of such changes. A reaction frequently quoted as being one of the most thoroughly investigated and typical examples of a termolecular transformation, and one which has never been seriously called in question, is that under discussion.

In their investigation of this reaction Noyes and Cottle (*loc. cit.*)

obtained velocity coefficients by the use of an erroneous formula (compare previous page).

Substitution of their data in the correct equation gives values which are far from constant, as can be seen from the following example.

$$a = [H{\cdot}CO_2Na] = 0{\cdot}050\ N;\ b = [CH_3{\cdot}CO_2Ag] = 0{\cdot}100\ N.$$

t (mins.).	$b - x$.	k_3 (Noyes and Cottle).	k_3 (corrected).
2	0·08103	30·0	26·2
4	0·07180	30·2	23·5
7	0·06395	21·2	20·6
11	0·05920	29·7	16·9
16	0·05625	28·0	13·5

These facts suggested inaccuracy in their experimental work, which, although correct in outline, may be criticised on one or two points.

To begin with a matter of minor importance, the temperature at which they carried out their experiments was the boiling point of water under the atmospheric pressure, and although, owing to the short duration of a single experiment, the error thus introduced would not be appreciable except in the comparison of the velocity coefficients of the various experiments, yet an ordinary change in pressure might result in an error of 10% in the coefficients.

Whilst excessively slow reactions cannot be relied on to give satisfactory results, it must also be recognised that very quick reactions are subject to great experimental error. There was no need for these investigators to perform their experiments at 100°, with consequent times of half-decomposition of the order of a few minutes; a temperature of 75° gives a velocity at once convenient from the point of view of the time required and capable of accurate measurement.

The method of titration employed by Noyes and Cottle is liable to slight inaccuracy on account of difficulties in the quantitative filtration of the finely-divided suspension resulting from the addition of the reaction mixture to the thiocyanate solution. The author considers that the error thus introduced may account, at least in part, for the apparently abnormal data obtained by these investigators.

It need scarcely be emphasised that their experiments afford absolutely no proof that the reaction is of the third order.

Re-investigation of the Reaction.

The procedure was as follows. Solutions of the two salts at the same temperature (74·97° ± 0·02°) were rapidly mixed in such proportions that the resulting solution was of a known concentration with regard to each. One solution was placed in a boiling tube,

A, which was fitted with a syphon tube, leading to the bottom of a similar vessel, *B*, containing the other solution, and also with an inlet tube through which air could be passed to force the liquid from *A* into *B*. The apparatus was standardised in order to allow for the small quantity of solution unavoidably remaining in vessel *A* and in the syphon tube. At a definite time after the two had been mixed and thoroughly agitated by a current of air, an analysis sample of about 10 c.c. was withdrawn, and rapidly cooled in ice. As it was essential to remove the insoluble products of reduction before titration, a very small filter-paper was well washed with 2 c.c. of the cooled solution and the remainder was filtered through it. Attention to the size of paper and the preliminary washing was necessary to reduce the loss due to adsorption of silver salt during filtration. 5 C.c. of the filtered solution were titrated with potassium thiocyanate, ferric alum being used as indicator, the accuracy being 0·02 c.c. Consideration was given to various possible sources of error, such as the colloidal products of reduction not retained by the filter and dissolved by the nitric acid in the indicator solution, and the change in normality of the solutions on heating to 75°.

Silver acetate and sodium formate give alkaline solutions, and as the change to an acid reaction, which takes place during the course of an experiment, might have introduced disturbances, experiments were performed in which varying amounts of acetic acid were added initially. Since the results with and without acid were sensibly the same, this precaution was not considered essential.

The tables of results give the velocity coefficients calculated from the correct formula in the column headed k (correct), and, for comparison, those obtained by the use of Noyes and Cottle's formula under the heading k(N. and C.). The correct formula, $dx/dt = k(a - x/2)(b - x)^2$, where a and b are the total initial normalities of sodium formate and silver acetate, respectively, and x is the fall in normality of silver acetate in time t, gives on integration

$$k = \frac{2}{(2a - b)^2 t}\left\{\frac{(2a - b)x}{b(b - x)} + \log_e \frac{2a(b - x)}{b(2a - x)}\right\},$$

while Noyes and Cottle's equation $dx/dt = k(a - x)(b - x)^2$, where a, b and x have the same significance as above, gives

$$k = \frac{1}{(a - b)^2 t}\left\{\frac{(a - b)x}{b(b - x)} + \log_e \frac{a(b - x)}{b(a - x)}\right\}.$$

The values of x given are calculated from the mean titration figures of from three to six experiments for each concentration. The accuracy obtained can best be shown by comparing the figures

for a single concentration : t is the time in minutes, s the values (c.c.) from a single experiment, and r the average of three experiments.

$$[HCO_2Na] = 0{\cdot}05N\,;\quad [CH_3{\cdot}CO_2Ag] = 0{\cdot}05N.$$

t	20	40	70	100	160	240
s	8·98	7·19	5·58	4·55	3·28	2·37
r	8·97	7·19	5·59	4·56	3·28	2·41

Tables of Results.

$$a = 0{\cdot}100\,;\ b = 0{\cdot}050.$$

t (mins.).	x.	k (corr.).	k (N. and C.).	t (mins.).	x.	k (corr.).	k (N. and C.).
20	0·0218	8·28	8·92	100	0·0395	8·84	10·81
40	0·0299	8·26	9·32	160	0·0433	9·79	12·55
60	0·0344	8·36	9·75	240	0·0460	11·94	15·98

The initial concentrations and the ranges of k (corr.) and k (N. and C.) in three similar experiments were :

$a = 0{\cdot}050$,	$b = 0{\cdot}050$,	k (corr.) = 8·45—10·25,	k (N. and C.) = 9·40—21·77
0·050,	0·025,	9·49—11·46,	9·75—13·73
0·025,	0·050,	8·61— 9·48,	9·64—32·52*

* These figures refer only to the first half of the reaction, as Noyes and Cottle's formula cannot be applied after the point of half-decomposition (compare p. 889).

Values calculated from the bimolecular formula are in all cases far from constant.

The following table gives the velocity coefficients, calculated from the correct formula, corresponding to the times of half-decomposition.

a	0·100	0·050	0·050	0·025
b	0·050	0·050	0·025	0·050
k	8·3	8·5	9·7	9·4

These figures indicate that, whilst the reduction of a silver salt in dilute solution by a formate is not a rigid termolecular reaction, yet, both from the point of view of the constancy of the values in any one experiment and from the slight variation in the magnitude of the constant with change in initial concentration of the reactants, it appears that the reaction is essentially one of the third order.

Summary.

The correct velocity equation has been deduced for those termolecular reactions in which two molecules of one of the reactants take part in the change.

Definite proof has been advanced that the reduction of silver acetate by sodium formate is essentially a reaction of the third order.

The author wishes to express his indebtedness to Professor Sir James Walker for the interest he has taken in this work and for much helpful criticism and advice.

UNIVERSITY OF EDINBURGH. [*Received, January 27th*, 1926.]

CXXIII.—*The Relative Concentrations of Various Electrolytes required to salt out Soap Solutions.*

By JAMES WILLIAM MCBAIN and ALBERT VINCENT PITTER.

IN a series of papers from this laboratory on the soap-boiling processes, it has been shown that there is a remarkable family likeness between the various soaps, whether pure, mixed or commercial, and that they differ in degree rather than in kind (McBain and Burnett, J., 1922, **121**, 1320; McBain and Langdon, J., 1925, **127**, 852; McBain and Elford, this vol., p. 421; McBain and Walls, *Fourth Report on Colloid Chemistry of the Brit. Assocn. for the Advancement of Science*, 1922, 244; McBain, Chap. in Vol. I of J. Alexander's forthcoming treatise on Colloids).

It has been shown that the phase-rule equilibria for each soap or mixture of soaps are affected in the same way by various salts; so that numerical ratios exist between the concentrations of individual salts required to produce the same effect upon any soap. Further, the effects in a mixture of electrolytes are additive. Likewise, the behaviour of a mixture of soaps seems to be approximately that expected from their respective constituents, apart from formation of curd or crystals.

Hence in order to be able to predict the concentration of any salt, or mixture of salts, required to obtain a specified equilibrium in any soap or mixture of soaps, two things are necessary. First, sufficient points must be established for the phase-rule diagram of each pure soap, using any one salt. Second, the numerical ratios between the concentrations of various salts required to produce a given salting out must be established with one concentration of any one soap. It is the object of the present communication to obtain the numerical ratios between various salts, using in every case $0{\cdot}25N_w$(weight normal)-sodium palmitate and making the definite comparison at 90°.

EXPERIMENTAL.

The method used has been sufficiently described in the papers previously mentioned. It depends on the separation of two isotropic liquid layers from one homogeneous liquid on gradual cooling from high temperatures.

0·25N_w-Sodium palmitate solutions were sealed up in strong glass tubes with various weights of specimens of the purest salts obtainable, and heated (in many cases far above the boiling point) until the contents of the tube were seen to be clear and perfectly homogeneous. They were then cooled slowly in a bath of glycerol until separation occurred. The experiments were carried out at different times during the past 5 years by C. S. Adams, L. S. Staddon, and the authors, with different samples of sodium palmitate, but the whole work was repeated this year by one of us (A. V. P.), using three different specimens of soap.

The results are in the following tables, all the qualitative observations of appearance, etc., being suppressed for lack of space.

Concentrations are given in every case in weight normality (N_w) defined here as g.-mols. (not equivalents) per 1000 g. of water. The data are also given in g. per 100 g. of total system.

Table I gives results obtained with a sample (*a*) of ordinary sodium palmitate obtained from Messrs. Kahlbaum in March, 1925. It was shown to be the sodium salt of a mixture of fatty acids of mean molecular weight about half-way between palmitic and stearic.

Table II gives results obtained with a sample (*b*) of pure sodium palmitate specially prepared by Messrs. Kahlbaum in September, 1925. Analysis showed it to contain 0·0081 equivalent excess alkali per mol.

Table III gives results (*c*) obtained by making up the systems with palmitic acid "Kahlbaum" and sodium hydroxide solutions, by the method of Bunbury and Martin (J., 1914, **105**, 417).

Table IV compares the concentrations of the various salts in mols. and in % by weight required to salt out at 90°, sodium chloride being taken as standard=1·00.

TABLE I.

Minimum concentrations of various salts required to salt out solutions of 0·25N_w-*sodium palmitate. March sample* (*a*)—*impure.*

Sodium hydroxide.

N ...	0·933	1·10	1·10	1·11	1·17	1·30
Temp.	—	87	87·1	90	105·5	131·2°

Sodium nitrate.

N_w ...	0·951	1·02	1·199	1·336
Temp.	80·7	108	151·8	173·6°

Sodium chloride.

N_w ...	0·873	0·913	0·915	0·942	0·985	1·004	1·098	1·099	1·253
Temp.	80·3	97·5	111	119·7	128·5	134·2	156·9	157·5	178·1°

Sodium acetate.

N_w ...	0·796	0·839	0·872	0·895	0·992	1·0471	1·12	1·23
Temp.	83	93	96·8	101	124·5	135·2	146	158°

TABLE II.

Minimum concentrations of various salts required to salt out solutions of 0·25N$_w$-sodium palmitate. September sample (b)—pure.

Sodium hydroxide.

N_w ...	0·994	1·130	1·214	1·303	1·337
Temp.	—	91·7	108	129·3	138°

Sodium nitrate.

N_w ...	1·05	1·110	1·22	1·302
Temp.	87	114	148·9	164·3°

Sodium chloride.

N_w ...	0·955	0·971	0·999	1·110	1·199
Temp.	89·6	98·5	105·5	135·3	157°

*Sodium iodide.**

N_w ...	0·802	0·844	0·872	0·887	0·905	0·987
Temp.	67·4	70·4	74·2	75·5	89·5	106·5°

Sodium bromide.

N_w ...	0·865	0·895	0·920	0·955	0·966	0·986	0·982	1·109	1·20
Temp.	77	92	93	109·3	111·5	118	120·4	154·5	172°

Sodium acetate.

N_w ...	0·821	0·900	0·966	1·00	1·063	1·128	1·305
Temp.	75	91·7	102·5	108	123	133	154°

Sodium carbonate.

N_w ...	0·887	0·897	0·933	0·953	0·983	0·995	1·064	1·064	1·107
Temp.	90	91	106·7	110·8	118	120·3	136	137·6	143

N_w ...	1·157	1·211	
Temp.	153	159·6°	

Sodium sulphate.

N_w ...	0·826	0·904	0·963	0·997	1·074	1·11	1·18
Temp.	90	103·5	119·7	134	147·5	151·6	164·5°

Sodium tungstate.

N_w ...	0·651	0·700	0·738	0·801
Temp.	93·8	114·4	132	153°

Sodium tartrate.

N_w ...	0·634	0·676	0·699	0·757	0·778	0·790	0·903
Temp.	85	104·5	115	137·2	141	151·5	176°

* A different sample of sodium palmitate was used in this case.

TABLE III.

Minimum concentrations of various salts required to salt out solutions of 0·25N$_w$-sodium palmitate. Pure samples (c) prepared from palmitic acid "Kahlbaum" and sodium hydroxide solution.

Sodium hydroxide.

N_w ...	1·097	1·127	1·253	1·341
Temp.	86·3	97·3	121	138·4°

Sodium chloride.

N_w ...	0·965	1·00	1·017	1·044	1·116	1·199
Temp.	92·6	105·5	114	120	140·7	161°

Sodium thiocyanate.

N_w ...	0·757	0·814	0·950	1·027
Temp.	86	110·5	146	173·3°

TABLE IV.

Minimum concentrations of various electrolytes (hydroxide and salts of sodium) required to salt out $0{\cdot}25N_w$*-solutions of sodium palmitate at* 90° (*sodium chloride* = 1·00).

Electrolyte.*	Mol. wt.	Concn. reqd. N_w.		% by wt.	Ratio. $N_w : N_w$.		% : %.
Hydroxide	40·01	(1·110)	(a)	3·99	1·24		0·86
		1·127	(b)	4·05	1·18		0·82
		1·106	(c)	3·97	1·16		0·80
					Mean 1·19	Mean	0·83
Nitrate	85·01	(0·970)	(a)	7·16	1·08		1·54
		1·056	(b)	7·74	1·11		1·56
					Mean 1·10	Mean	1·55
Chloride	58·45	(0·895)	(a)	4·66	1·00		1·00
		0·953	(b)	4·95	1·00		1·00
		0·955	(c)	4·96	1·00		1·00
					Mean 1·00	Mean	1·00
Iodide	149·9	0·905	(d)	11·27	0·95		2·19
Bromide	102·9	0·898	(b)	7·95	0·94		1·61
Acetate	82·02	(0·838)	(a)	6·03	0·94		1·30
		0·895	(b)	6·42	0·94		1·30
					Mean 0·94	Mean	1·30
Carbonate	106·0	0·887	(b)	8·08	0·93		1·63
Sulphate	142·1	0·826	(b)	9·89	0·87		2·00
Thiocyanate	81·07	0·763	(c)	5·46	0·80		1·10
Tungstate	294	0·645	(b)	15·1	0·68		3·04
Tartrate	194·3	0·645	(b)	10·46	0·68		3·12

(a) = March sample of sodium palmitate (impure).
(b) = September sample of sodium palmitate (pure).
(c) = Sodium palmitate prepared from palmitic acid "Kahlbaum" and sodium hydroxide.

* Sodium fluoride also was tested, but it was not sufficiently soluble to salt out the palmitate at 90°.

The electrolytes used, with the exception of sodium thiocyanate, were dried by heating at 120—130°. The sodium thiocyanate was dried to constant weight in a vacuum over calcium chloride at room temperature.

All our numerical results are summarised in Table IV, showing the absolute and relative amounts of the various electrolytes required to salt out sodium palmitate at 90°.

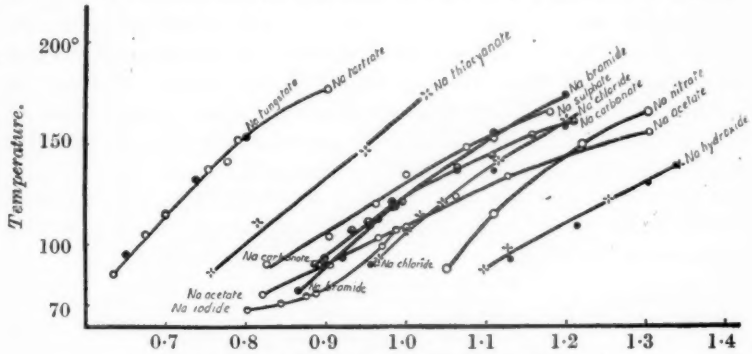
The only published data of sufficient accuracy by which to check our results are those from the Karlsruhe laboratory, which are based upon ratios obtained by Richert (*Dissert.*, Karlsruhe, 1911) for carbonate and hydroxide. He found, for various soaps, that 1·01 mols. of carbonate and 1·27 equivalents of hydroxide had the same effect as 1 equivalent of sodium chloride, whereas we have found 0·93 and 1·19, respectively. The divergence from our results amounts to about 6%.

To show the effect of temperature upon the various electrolytes the results have been plotted in Fig. 1. The figure shows that the ratios are not quite constant and independent of temperature, although the deviation does not exceed about 6%. This gives a second measure of the extent to which these data are generally valid, and they are borne out by an analysis of our unpublished data on commercial oils and fats as well as other results from the Karlsruhe laboratory and also the well-known data of Merklen.

An immense amount of information can be derived from these approximate numerical ratios which enables prediction to be made, well within 10%, of the maximum concentration of salts which

FIG. 1.

Concentrations of electrolytes required to salt out $0{\cdot}25N_{w}$*-sodium palmitate.*



(*The crosses indicate results obtained with solutions made up from palmitic acid "Kahlbaum."*)

may be added to any soap solution without salting it out. They enable all the complicated mixtures used in commercial soap boiling to be reduced to a common basis for comparison and control. Taken in conjunction with the equilibrium diagrams now becoming available for pure and commercial soaps, whether derived from sodium or potassium, they facilitate the approximate prediction of the concentration of any mixture of electrolytes required to produce a given effect.

Perhaps the most unexpected feature of Table IV is that, as a first approximation, the salts do not replace each other equivalent for equivalent, but rather mol. for mol. irrespective of their valency. For example, sodium thiocyanate comes, in this respect, between sodium sulphate and sodium tungstate; and one mol. of sodium carbonate exactly replaces one equivalent of acetate or iodide.

The results here discussed bear no relation whatsoever to the

Hoffmeister series, as may be seen from the order of the electrolytes in Table IV. Equally, the results are at variance with what might have been expected from the equation of the Donnan equilibrium, since here the order of the electrolytes is irrespective of their valency.

The most comparable factor common to all the salts seems to be the concentration of the sodium ion. Although no data are available for the actual mixtures in the soap solutions, yet this point may be brought out from an examination of such conductivity data for aqueous solutions of pure electrolytes as are given in Landolt-Börnstein-Roth's "Tabellen." The concentration of the sodium ion for all the electrolytes except the acetate, thiocyanate, carbonate, tartrate, and hydroxide is almost exactly two-thirds normal, whereas for these five cases it is $0{\cdot}5N_w$, $0{\cdot}54N_w$, $0{\cdot}58N_w$, $0{\cdot}76N_w$, and $0{\cdot}8N_w$, respectively. It is clear, therefore, that the equilibria are not exclusively determined by the degree of dissociation into sodium ion, although this is predominant. Matters are not improved by an attempt to substitute for concentration of sodium ion, its activity. The data are available for the chloride and hydroxide and the activities are proportional to the total concentrations required to produce the same effect, whereas they should have been inversely proportional, thus revealing a discrepancy of about 40%.

Summary.

1. Measurements have been made of the relative salting-out action of eleven different electrolytes on soap solutions.

2. With the aid of numerical ratios derived therefrom it is possible to compare, predict, and control all the various equilibria obtained with pure and commercial soaps with any mixture of electrolytes to within an accuracy of about 5 to 10%.

UNIVERSITY OF BRISTOL. [*Received, January 25th*, 1926.]

CXXIV.—*Hydrofluozirconic Acid and the Analysis of Zirconium Fluoride.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and EDWIN CLAXTON ROPER.

THIS investigation was undertaken with the object of verifying, or disproving, the existence of an acid fluoride of zirconium, or a hydrofluozirconic acid. Preliminary work on the ordinary hydrated fluoride led to results which do not altogether agree with those previously recorded. These previous results, so far as they are

relevant, may be summarised as follows. The evaporation of a solution of zirconium dioxide in hydrofluoric acid yields triclinic tablets, which, when dried to constant weight in air, consist of the trihydrate, $ZrF_4,3H_2O$ (Chauvenet, *Compt. rend.*, 1917, **164**, 727). This compound begins to be dehydrated at 100°; at 140° it loses 2 mols. of hydrogen fluoride, giving the dihydrate $ZrOF_2,2H_2O$, and above 140° it becomes converted into $ZrOF_2$. In the cold, this absorbs hydrogen fluoride, giving the monohydrate or $ZrOF_2,2HF$. A solution of the latter in water slowly deposits a substance which, when dried to constant weight, has the composition $ZrOF_2,2H_2O$, and at 120° is converted into $ZrOF_2$.

Our experience supplements, and leads us to criticise, these results. Evaporation of solutions containing fluorides of zirconium yields only powders of indefinite composition, unless the evaporation is carried out at the ordinary temperature and under reduced pressure. The large crystals thus obtained cannot be dried in air to constant weight without decomposition of the surface layer, since they continually give off hydrogen fluoride. They must therefore be dried quickly and kept enclosed in waxed tubes. Compounds intermediate between the trihydrate and the oxyfluoride may exist, but the isolation of these would require a careful study of the partial pressures of hydrofluoric acid and water. Compounds of constant composition are not likely to be isolated simply by drying or heating to constant weight in contact with the atmosphere. The oxyfluoride is not obtained by heating the trihydrate in air above 140° for any reasonable time; the weight may become constant, but is greater than is required for this compound (*vide infra*). Further, it cannot be considered that the composition of any of these compounds is established by means of the zirconia content alone. There is no evidence in the work of Chauvenet (*loc. cit.*) that any analysis has been attempted beyond the obvious and comparatively easy estimation of zirconia. We have found that none of the methods of estimating hydrogen fluoride was satisfactory in the presence of dissolved zirconium compounds. It has been necessary to devise a new method, which was first tested with potassium hydrogen fluoride and then applied to the best authenticated compound, $ZrF_4,3H_2O$. This compound, crystallised under the conditions mentioned above, appears as transparent or translucent, polygonal plates, the sides of which contain characteristic angles, 109°, 113°, 121°, 126° $\pm$ 1°.

Analysis.—The calcination of this compound to oxyfluoride, with subsequent ignition to dioxide, requires some care, since a part may sublime, if it is heated too rapidly, either as the oxyfluoride or the tetrafluoride. After being gently heated in a covered crucible,

it was converted into the sulphate and then ignited to constant weight. Freshly-prepared crystals gave, as the mean of five analyses, 36·3% Zr, the extreme values being 34·4 and 38·0%. They thus appear to be more highly hydrated than the trihydrate, which requires 41·0%, or even than the tetrahydrate, which would require 38·0% Zr. Later preparations agreed more closely with the composition of the trihydrate. The necessity for determining another constituent was evident, and an apparatus was constructed in which the hydrogen fluoride could be volatilised. This consisted of a copper tube having an internal diameter of about ½ inch, which was cut with a special reamer and ground to fit a conical platinum stopper. This was continued as a platinum delivery tube which dipped in standard alkali. The platinum boat containing the compound to be analysed was placed in the copper tube close to, and partly entering, the platinum stopper. A current of dry air, or, in later experiments, superheated steam, was passed through the tube. The hydrofluoric acid evolved was absorbed in the alkali without loss, as was proved by analyses of potassium hydrogen fluoride.

Results of Analysis.—Samples A and B were prepared at different times but had the same composition. The rest were all taken from one preparation. A was first heated in air, the rest in steam. The relatively small amount of hydrogen fluoride which can be obtained by heating in air is noteworthy. The manner in which hydrolysis proceeds during the heating was determined by weighing the residues and titrating the hydrofluoric acid at various stages. When the compound was heated in dry air it lost hydrogen fluoride, which was formed by hydrolysis with the contained water, and also some of this water. The residue, when heated in undried air, lost no appreciable weight but gave off more hydrogen fluoride. In this case, more of the fluoride must have been hydrolysed, but by external water, some of which was retained: $ZrF_4+H_2O = Zr(OH)F_3+HF$.

A portion of the residue was ignited to dioxide as described above. The hydrogen fluoride driven off by this operation may be calculated on the assumption that the compound is hydrolysed (*a*) by its own water, or (*b*) by external water. These two estimates, when added to the hydrofluoric acid titrated, furnish the two values in the last line of the table. The uncertainty arises from the fact that it is not possible, by the strongest heating which the apparatus permitted (between 300° and 400°) in a current of air, to drive off all combined hydrogen and to convert all the compound into $ZrOF_2$. The ratio of the weight of zirconia to that of the product heated in the tube was 0·77 instead of 0·8473 = $ZrO_2/ZrOF_2$. When steam was used the hydrolysis was more complete. Sample C lost both hydrogen fluoride and water, the ratio of ignited zirconia to steam-

heated product being now 0·823. In the case of sample D, the ratio was 0·836. The percentages of hydrogen fluoride will accordingly be nearer to the higher value in the table. In order to obtain a direct titration of still more hydrofluoric acid, we arranged to hydrolyse at a higher temperature. A small platinum tube, closed at one end by a cap of platinum foil, was placed inside the platinum delivery tube, which was heated to bright redness in a current of superheated steam. Samples B and F were analysed by this method. Sample B yielded 34·0% of hydrogen fluoride when heated in steam below a red heat and a further 3·48% when heated to a bright red heat. The weight of the residue showed that it had been almost completely hydrolysed to oxide. In calculating the results, the quantities of zirconia and hydrogen fluoride were added together, and the water was obtained by difference.

	A.	B.	C.	D.	E.	F.
% ZrO_2	58·8	57·6	53·9	54·0	(54)	(54)
% HF (titrated)	8·2	37·5	19·8	22·3	31·2	31·1
% HF total	25·7–	—	30·5–	32·9–	—	—
(estimated)	37·8	37·5	39	41·5	—	—

The weighted mean of the zirconia in A and B is 58·5, the hydrogen fluoride is 37·5, the water 4·0; the composition therefore corresponds to $ZrF_4,2{\cdot}45H_2O$. The preparation containing 54% of zirconia contains at least 31% of hydrogen fluoride in C and more than 33% in D. We estimate it at 35%, for the reason mentioned on previous page. The water will therefore be 11·0, corresponding to $ZrF_4,3{\cdot}4H_2O$. Thus the crystals do contain the tetrafluoride, but the water of crystallisation is proved to be variable.

The Acid Fluoride.—Numerous double fluorides have been prepared such as $2NH_4F,ZrF_4$; $3NH_4F,ZrF_4$; KF,ZrF_4,H_2O; $2KF,ZrF_4$ (Marignac, *Ann. Chim. Phys.*, 1860, **60**, 271); also $2NaF,ZrF_4$ (Wells and Foote, *Amer. J. Sci.*, 1866, **3**, 466). The salt $2KF,ZrF_4$ is one of the easiest to prepare, yet even in this case a slight excess of potassium fluoride produces $3KF,ZrF_4$. The free acid might correspond to any of these salts. An acid salt is said to be deposited on rubbing the walls of a vessel containing a solution of zirconia in hydrofluoric acid (Fischer and Thiele, *Z. anorg. Chem.*, 1910, **67**, 309). This dissolved readily in water, but with difficulty in concentrated hydrofluoric acid. When treated with lead carbonate, it gave a soluble lead salt which was believed to be $PbZrF_6$. Some soluble lead salt is certainly formed when lead carbonate is added to any solution containing zirconium fluoride, for, after removal of the lead fluoride by filtration, more lead may be precipitated from the filtrate by means of hydrogen sulphide, and the second filtrate contains both zirconium and fluorine.

A hydrofluozirconic acid is also said to be produced when hydrogen fluoride is absorbed by zirconium tetrafluoride (Chauvenet, *loc. cit.*). The isolation of an acid by either of these methods would appear to be difficult. We consider that the only method which offers any reasonable chance of success is to add much anhydrous hydrogen fluoride to a little zirconium fluoride which is already in solution.

Preparation.—The anhydrous acid, prepared by distilling dry sodium hydrogen fluoride in a copper still, was condensed in a platinum bottle or crucible which fitted into a copper receiver. After addition of this to the solution of zirconium fluoride or *vice versa*, a fine, white crystalline solid was usually deposited. This was cooled in a freezing mixture and well stirred. The liquid was then decanted, and the solid washed several times by decantation with dry ether and pressed on filter-paper. This substance has been prepared on five occasions. The appearance of the crystals was always the same, but very different from that of the ordinary fluoride. Under the microscope, they were seen to be of uniform type—long prisms with chisel-shaped ends. On exposure they gave off hydrogen fluoride and became dull on the surface. In a few days the whole crystal became opaque. When they were dissolved in a very little water (in which they are extremely soluble) and treated with a few drops of lead acetate, the liquid remained clear. A drop of hydrofluoric acid produced an immediate turbidity. The hydrofluozirconic acid was therefore not much hydrolysed.

Analysis of the Acid Fluoride.—One of the earlier samples, weighed rapidly in a closed platinum crucible with a tightly fitting lid and then converted into zirconia, contained 46·0% ZrO_2. In the case of the last sample, we were able to determine the hydrogen fluoride separately as described above, and to follow the course of the decomposition: (1) 0·4603 g. was heated in a current of dry air. The loss was 0·1359 g., of which 0·0772 g. was hydrogen fluoride. (2) The residue, 0·3244 g., was heated in steam. The loss was 0·0379 g., and the hydrogen fluoride 0·03619 g. This is the stage in which the hydrolysis proceeds at the expense of water of crystallisation. (3) A portion, 0·0863 g., of the last residue, when heated in steam to a bright red heat, lost 0·0196 g. The hydrogen fluoride was 0·01962 g. (4) Another portion, 0·0911 g., ignited with sulphuric acid, gave 0·0682 g. of dioxide. All quantities being referred to the original weight, the hydrogen fluoride lost in (3) is 0·0658 g., whilst the total loss in (4) is 0·0720 g. Since steaming at a red heat causes conversion nearly into ZrO_2 with a little $ZrOF_2$, the final loss, 0·0720 − 0·0658 = 0·0062 g., represents hydrogen fluoride produced by the reaction $ZrOF_2 + H_2O = ZrO_2 + 2HF$, the water being derived from external sources such as the sulphuric acid. This loss must corre-

spond to a weight of hydrogen fluoride = $40 \times 0{\cdot}0062/22 = 0{\cdot}0113$ g. The weight of zirconia calculated on the original weight of compound is 0·215 g., or 46·59%. On heating in dry air, 1 mol. of the compound loses rather more than 2 mols. of hydrogen fluoride and rather less than 2 mols. of water. On heating in steam, it loses rather more than 1 mol. of hydrogen fluoride, and, at a bright red heat, rather less than 2 mols. of the acid.

Composition of the Acid.—0·4603 G. gave 0·1792 g. HF (titrated) and 0·0113 g. (deduced from final loss of weight), total 0·1905 g.; and 0·0548 g. of H_2O (by difference). The simplest formula calculated from these results is $ZrF_4,1{\cdot}5HF, 3{\cdot}74H_2O$, or $ZrOF_2,3{\cdot}5HF, 2{\cdot}74\ H_2O$. On account of the difficulty in avoiding loss of hydrogen fluoride during the weighing, etc., and of the hygroscopic character of the compound, we consider that, as originally precipitated, it would probably contain the extra 0·5 mol. of hydrogen fluoride and 0·75 mol. less water, and that it would be hydrofluozirconic acid corresponding to the best known potassium salt, with the addition of about 3 mols. of water of crystallisation, *i.e.*, $H_2ZrF_6,3H_2O$.

One of us (E. C. R.) desires to acknowledge the continuance of a maintenance grant from the Department of Scientific and Industrial Research which enabled this work to be completed. We also desire again to record our indebtedness to the Royal Society for a former grant towards the purchase of apparatus.

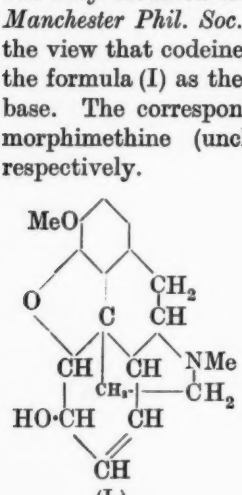
UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, December 14th.* 1925.]

CXXV.—*The Morphine Group. Part III. The Constitution of Neopine.*

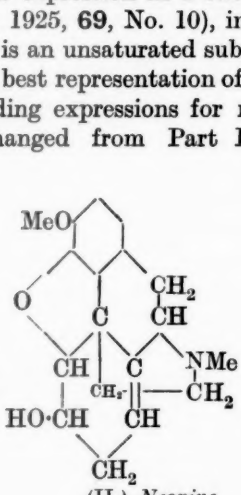
By CONSTANT FREDERIK VAN DUIN, ROBERT ROBINSON, and JOHN CHARLES SMITH.

THE rare opium alkaloid which is the subject of this communication was discovered by Messrs. T. and H. Smith of Edinburgh in the final mother-liquors from the isolation of opium alkaloids and separated in the form of its readily crystallisable hydrobromide. Dobbie and Lauder (J., 1911, **99**, 34) investigated this salt and the amorphous base which could be obtained from it and concluded that neopine is a hydroxycodeine. We found that neopine hydrobromide, for a supply of which we are greatly indebted to Messrs. T. and H. Smith, possessed the properties described by Dobbie and Lauder. The analysis, however, gave the formula $C_{18}H_{22}O_3NBr$ instead of $C_{18}H_{22}O_4NBr$ required for a hydroxycodeine hydro-

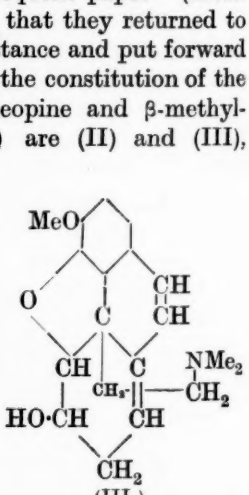
bromide. The free base was obtained in a crystalline condition, m. p. 127·5° (corr.), and was found to have the formula $C_{18}H_{21}O_3N$. It appeared to be an isomeride of codeine and this was confirmed by the examination of several derivatives. Moreover, like codeine, neopine contains one methoxyl group, one alcoholic hydroxyl group, and one methyl group attached to nitrogen. The close relation of the base to codeine is brought out in a very clear light by the fact that catalytic hydrogenation of neopine leads to the formation of dihydrocodeine. It will be recalled that the decomposition of codeine methohydroxide leads to the formation of α-methylmorphimethine, which is changed to an isomeric β-methylmorphimethine by means of boiling alcoholic potassium hydroxide. The decomposition of neopine methohydroxide gives at once pure β-methylmorphimethine. Neopine is thus to be regarded as β-codeine; it stands to codeine in the same relationship that β-methylmorphimethine bears to α-methylmorphimethine. In Parts I and II of this series (J., 1923, **123**, 980, 998) Gulland and Robinson suggested a new formula for codeine, but they modified this expression in a subsequent paper * (*Mem. Manchester Phil. Soc.*, 1925, **69**, No. 10), in that they returned to the view that codeine is an unsaturated substance and put forward the formula (I) as the best representation of the constitution of the base. The corresponding expressions for neopine and β-methylmorphimethine (unchanged from Part I) are (II) and (III), respectively.



(I.)



(II.) *Neopine.*



(III.)

* This paper was read at a meeting of the Manchester Literary and Philosophical Society on February 7th, 1925, and a statement of the proposed change in the morphine formula was given in an abstract in *Nature* (1925, **115**, 625). The memoir could be purchased in a separate form in July, 1925. About the same time, Wieland and Kotake (*Annalen*, 1925, **444**, 69) emphasised the unsaturated nature of codeine and located the double bond in the new position also adopted by Gulland and Robinson. The above particulars are contributed in order to prove that the suggestions of Gulland and Robinson and of Wieland and Kotake were independent and contemporaneous.

The existence of a β-codeine might be anticipated on the basis of many codeine formulæ, but it should be noted that neopine is less readily oxidised by permanganate and also less readily catalytically hydrogenated than codeine. Any hypothesis, therefore, of the relation of codeine to neopine or of α- to β-methylmorphimethine which suggests that codeine has a bridge ring that becomes an ethylene linking in neopine is definitely opposed to the facts. The only possible conclusion that can be drawn from the circumstance that neopine is more stable than codeine towards reagents for the ethylene linking is that the latter contains a double bond which moves, in the transformation of α-methylmorphimethine to the β-isomeride, to a more sheltered position or at least to a position in which it exhibits a smaller degree of reactivity.

Experimental.

Neopine Hydrobromide.—The substance provided by Messrs. T. and H. Smith was anhydrous and remarkably homogeneous. It darkened from about 240°, became very dark at 279°, blackened at 281°, and melted with decomposition at 282—283° (Found: Br, by titration, 21·1. $C_{18}H_{22}O_3NBr$ requires Br, 21·0%). The salt was dried at 100° for 5 hours (Found: Br, 21·1%); it was then recrystallised and dried at 100° for 5 hours (Found: Br, 21·1%). The identity of the material with that examined by Dobbie and Lauder (*loc. cit.*) is evident from the determination of the rotatory power. The salt supplied by Messrs. T. and H. Smith dried at 100° for 5 hours had $[\alpha]_D^{24°}$ + 17·08° in aqueous solution ($c = 5·152$). After recrystallisation and drying at 100°, we found $[\alpha]_D^{24°}$ + 17·32° ($c = 3·696$). Dobbie and Lauder found $[\alpha]_D^{20°}$ + 17·07° ($c = 5·1884$) and $[\alpha]_D^{20°}$ 17·4° ($c = 5·0741$).

Neopine.—The hydrobromide was dissolved in water, decomposed by the addition of sufficient concentrated aqueous potassium hydroxide to produce an emulsion (the base is rather readily soluble in water), and the neopine thrice extracted with benzene. The benzene solutions were dried with potassium carbonate and evaporated, leaving a soft varnish. This was dried at about 80° and after some hours a crystal nucleus was noticed. On cooling and scratching, the whole varnish crystallised and the crude product had m. p. 125°. The base is best recrystallised from light petroleum (b. p. 80—100°) and separates in long, glistening, brittle, colourless needles, m. p. 127—127·5° (corr.) (Found in material heated at 80°: C, 72·4; H, 7·1; N, 4·6, 4·7*, 4·7*; MeO, 10·5*, 10·4*; NMe*, 5·2; *M* in camphor, 288. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0; N, 4·7; MeO, 10·4; NMe, 5·0%; *M*, 299).

* By micro-methods.

In aqueous solution ($c = 5{\cdot}1084$) the base is apparently optically inactive (D line at 20°), but on the addition of hydrochloric acid (Neop., HCl in 0·397*N*-HCl) the value $[\alpha]_D^{25°} + 18{\cdot}85°$ was observed. In dry chloroform ($c = 7{\cdot}4740$), we found $[\alpha]_D^{25°} - 28{\cdot}10°$ for the base. With the Froehde and Mandelin reagent, codeine and neopine give yellow colorations changing to blue; this change appears to be slower in the case of neopine. The alkaloid dissolves in water, and a very dilute solution does not immediately decolorise a drop of dilute aqueous potassium permanganate which is added to it. Under similar conditions, codeine rapidly reduces the oxidising agent.

Acetylneopine.—A hydroxycodeine has the same state of oxidation as thebaine, and before we were aware of the true composition of neopine an attempt to degrade it was made under the conditions of the preparation of diacetylthebaol from thebaine, but the result was negative. Neopine (4 g.) was acetylated in 2 hours with boiling acetic anhydride (15 c.c.) in presence of anhydrous sodium acetate (2 g.), and the resulting solution added to water and rendered alkaline by means of sodium carbonate. The base, isolated by means of ether, was obtained as a pale yellow varnish which has not yet been crystallised [Found: $CH_3{\cdot}CO$, 12·7 (by A. G. Perkin's method; J., 1905, **87**, 107). $C_{18}H_{20}O_3N{\cdot}CO{\cdot}CH_3$ requires $CH_3{\cdot}CO$, 12·6%]. Acetylneopine combines very readily with methyl iodide in methyl-alcoholic solution; the product crystallises from methyl alcohol in long, glistening needles which probably contain solvent of crystallisation, since they lose their lustre on heating. *Acetylneopine methiodide* darkens at 250° and has m. p. 256—257° (decomp.; corr.) (Found in material dried at 95—100° to constant weight: C, 52·4; H, 5·5; I, by titration, 26·15. $C_{21}H_{26}O_4NI$ requires C, 52·2; H, 5·4; I, 26·3%).

Catalytic Hydrogenation of Neopine with Formation of Dihydrocodeine.—The reductions were carried out at the ordinary temperature in a vessel filled with hydrogen and provided with a stirrer. Codeine (5 g.) dissolved in water (50 c.c.) and acetic acid (2 c.c.) absorbed in 25 minutes 385 c.c. of hydrogen in presence of colloidal palladium (from 10 c.c. of 0·5% palladous chloride *). This was equivalent to 370 c.c. at *N.T.P.* The volume theoretically required for the saturation of one double bond is 375 c.c. The isolated product had at first m. p. 55° and was dried at 110°. It then melted at 112—113° (corr.) after crystallisation from water containing a few drops of methyl alcohol. This was the highest value that could be obtained. Skita and Frank (*Ber.*, 1911, **44**, 2865) gave the m. p.

* The solution employed in both reductions contained also 0·5% of gum arabic.

of dihydrocodeine as 65°, whilst Freund (*J. pr. Chem.*, 1920, **101**, 12) gave 86—88°. Oldenburg (D.R.-P. 260,233) also quoted the value 62—63°. Mannich and Löwenheim (*Arch. Pharm.*, 1920, **258**, 304) showed that dihydrocodeine with $2H_2O$ melts at 55° or 88°, whilst the anhydrous substance has m. p. 111—112°. Wieland and Koralek (*Annalen*, 1923, **433**, 269) crystallised the base from 80% methyl alcohol, a process which we cannot repeat, and gave the m. p. 112—114°.

A solution of neopine (2·5 g.) in water (25 c.c.) and acetic acid (1 c.c.) containing colloidal palladium (5 c.c. of 0·5% palladous chloride) was stirred in hydrogen, when the palladium was at once flocculated. More palladous chloride solution (10 c.c.) was added, but flocculation again occurred. In about 15 hours, 180 c.c. of hydrogen were absorbed (equiv. to 176 c.c. at *N.T.P.*; calc., 185 c.c.). The base was rendered to chloroform from the filtered solution and, after removal of the solvent, the residual oil crystallised when inoculated with dihydrocodeine (variety, m. p. 55°). This material melted at 51—53°, but after resolidification it had m. p. 81—84° and after drying at 80° for 1 hour the m. p. was 110—111°. After crystallisation from water containing a few drops of methyl alcohol, the substance dried at 80° had m. p. 112—113° (corr.) (Found: C, 71·5; H, 7·9. Calc. for $C_{18}H_{23}O_3N$: C, 71·7; H, 7·7%). Approximately equal quantities of dihydrocodeine, m. p. 112—113°, and dihydroneopine, m. p. 112—113°, were melted together on a watch glass. The mixture rapidly crystallised on cooling and had m. p. 112—113°.

Conversion of Neopine into β-Methylmorphimethine.—Neopine combined rapidly with methyl sulphate in benzene solution to a *methosulphate*, which separated in a resinous condition. It was very deliquescent and readily soluble in water and on the addition of potassium hydroxide to the solution no precipitation occurred. On boiling, the methine suddenly made its appearance as oily drops, and these crystallised at once even in the hot liquid on the introduction of a crystal of β-methylmorphimethine. We are greatly indebted to Dr. R. S. Cahn for a specimen of pure β-methylmorphimethine. The neopinemethine crystallised from alcohol in large, twinned, rhombohedral prisms, m. p. 135°, and at the same temperature when mixed with β-methylmorphimethine. It dissolved in sulphuric acid to a deep crimson solution, which became royal blue on heating and on dilution with water, green and then yellow with an intense green fluorescence. This reaction is characteristic of β-methylmorphimethine.

Neopinemethine methiodide was prepared from the methine before the latter had been crystallised. The substance crystallised from

water in glistening needles, m. p. 291° (decomp.) after darkening from 260° (Found: I, 27·8. Calc., I, 27·9%). Knorr and Smiles (*Ber.*, 1902, **35**, 3010) and Knorr and Hawthorne (*Ber.*, 1902, **35**, 3012) found that β-methylmorphimethine methiodide had $[\alpha]_D^{17°}$ + 233° ($c = 0·6$) in 97% and 90% alcohol. Solutions of neopinemethine methiodide having a similar concentration crystallised on cooling, but we now know that neopinemethine is β-methylmorphimethine in an exceptionally pure condition. We found that neopinemethine methiodide had $[\alpha]_D^{21°}$ + 241·1° ($c = 0·506$) in absolute methyl alcohol and $[\alpha]_D^{21°}$ + 262·0° ($c = 0·3$) in 90% ethyl alcohol.

We desire to thank the Ramsay Memorial Trust for a Fellowship (Netherlands) which enabled one of us to take part in this investigation, and for a similar reason we are also grateful to the Royal Commissioners of the Exhibition of 1851 for a Scholarship.

THE UNIVERSITIES OF ST. ANDREWS AND MANCHESTER.

[*Received, February 3rd*, 1926.]

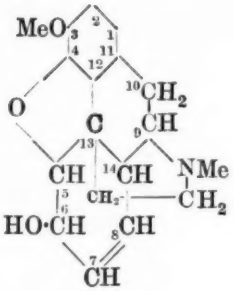
CXXVI.—*The Morphine Group. Part IV. A New Oxidation Product of Codeine.*

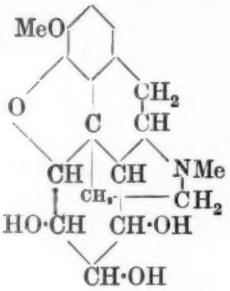
By ROBERT SIDNEY CAHN and ROBERT ROBINSON.

THE secondary alcohol codeine can be oxidised to the corresponding ketone by means of chromic acid or of potassium permanganate in acetone solution, and apart from the hydroxycodeine which accompanies codeinone in the former case (Ach and Knorr, *Ber.*, 1903, **36**, 3067) no other products of direct oxidation of the base have been described. This has perhaps led to the impression that the attack of oxidising agents is invariably on the alcoholic group, although attention has occasionally been directed to the fact that the sensitiveness of codeine to permanganate is greater than that of any known saturated alcohol and strongly suggests the existence of an ethenoid group in the molecule (compare Wieland and Kotake, *Annalen*, 1925, **444**, 69; Gulland and Robinson, *Mem. Manchester Phil. Soc.*, 1925, **69**, No. 10). The remarkable ease with which codeine may be converted into a dihydro-derivative by catalytic hydrogenation is in harmony with this hypothesis, and we now bring forward further evidence tending in the same direction. The action of potassium permanganate on codeine (I) in very dilute aqueous solution leads to the addition of two hydroxyl groups to the molecule and the product is dihydroxydihydrocodeine (II). This substance yields a basic triacetyl derivative and its form-

ation demonstrates the existence of an ethylenic linking in codeine. The position chosen for the double bond in (I) is that independently

(I.)





(II.)

selected by Wieland and Kotake and by Gulland and Robinson for different reasons. It is especially required to explain the codeine–ψ-codeine change (analogy to geraniol–linalool) and the reactivity of the chlorine atom of chlorocodide (analogy to allyl chloride and benzyl chloride). A possible objection (compare Gulland and Robinson, *loc. cit.*) is that ψ-codeinone reacts with benzaldehyde as if it contained the group $\cdot CH_2 \cdot CO\cdot$, whereas it should contain $\cdot O \cdot CH \cdot CH{:}CH \cdot CO\cdot$ on the suggested basis. The difficulty is removed by recognising the following system of tautomerides :

$$\cdot CH \cdot CH{:}CH \cdot CO\cdot \rightleftharpoons \cdot C{:}CH \cdot CH{:}C(OH)\cdot \rightleftharpoons \cdot C{:}CH \cdot CH_2 \cdot CO\cdot$$

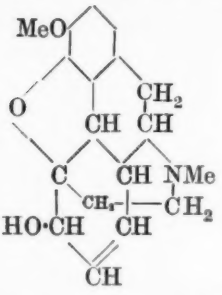
which might be equilibrated in presence of alcoholic potassium ethoxide or similar reagents. Although it seems probable that general agreement will soon be reached in regard to the occurrence of the group $\cdot CH(OH) \cdot CH{:}CH\cdot$ in codeine and its isomerides, and the morphine problem will be to that extent simplified, there is still room for differences of opinion in regard to the point of attachment of the ethanamine chain. Wieland and Kotake (*loc. cit.*) have noted that some substances which on the basis of (I) should contain the group $\cdot CH_2 \cdot CO \cdot CH_2\cdot$ nevertheless have only one reactive position * and prefer the formula (III) for codeine.

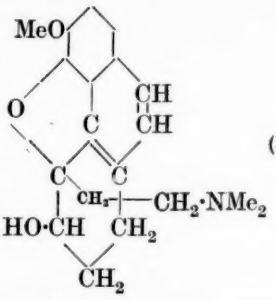
On the other hand, a consideration of the behaviour of the unsaturated centres in the methylmorphimethines appears to us to provide further evidence favouring the formula (I). If (III) represented codeine, we imagine that β-methylmorphimethine would be

* The attachment of the ethanamine chain in position 13, as in (I), was not based on the production of dipiperonylidene derivatives of thebainol and dihydrothebainone but on the arguments put forward in Part I of this series, to which, with the modification made in our note in the *Manchester Memoirs*, we adhere.—J. M. G., R. R.

(IV), a naphthalene derivative. That the bond migrating from the position 7—8 should halt in the position 8—14 and not proceed to

(III.)





(IV.)

13—14, where it assists in the formation of a new aromatic nucleus, seems highly improbable. Now β-methylmorphimethine appears to contain non-aromatic unsaturated centres, since it very readily reduces permanganate, more readily than neopine * does, and on catalytic hydrogenation gives a 9 : 10-dihydro-derivative (von Braun, *Festschr. phys. Ver.*, Frankfort a. M., 1924, Sept.; Cahn, *Dissert.*, Frankfort, 1925). The formula (I), on the other hand, affords a satisfactory explanation of the relations of codeine, neopine, and α- and β-methylmorphimethines.

EXPERIMENTAL.

Dihydroxydihydrocodeine (II).—An aqueous solution of potassium permanganate (332 c.c. of 1%) was added during 1·5—2 hours to a mechanically stirred solution of codeine † (10 g.) in water (1500 c.c.) mixed with ice (500 g.) and cooled in an ice-bath. The manganese dioxide was precipitated from the colloidal solution by passing carbon dioxide for ½ hour and stirring for a further equal period, and the almost colourless filtered liquid was then concentrated to about 400 c.c. by distillation under diminished pressure. Much frothing and decomposition occurred. By means of ether codeine (1·4—1·6 g.) was extracted from the dark brown solution, which was then concentrated to about 40 c.c. and treated with saturated aqueous potassium carbonate (150 c.c.), a semi-solid, almost black material being precipitated. The mixture was twice extracted with 200 c.c. of chloroform, and the solutions were dried with sodium sulphate and evaporated, leaving 5 g. of an amorphous, hygro-

* β-Methylmorphimethine is also neopinemethine (Van Duin, Robinson, and Smith, this vol., p. 903).

† A similar experiment was carried out with ψ-codeine, but necessarily in much more dilute solution owing to the sparing solubility of the base in cold water. A large fraction of the ψ-codeine was recovered and no other crystalline product was isolated.

scopic, dark brown residue (A), which was taken up in dry ethyl alcohol (15 c.c.). Crystallisation was induced by rubbing and after some hours the crude base (1·2 g. or 11·5%) was collected and twice recrystallised from absolute alcohol (yield 0·6 g.) in colourless, glistening, diamond-shaped plates, m. p. 208—209° (Found in material dried in a vacuum at 100°: C, 64·8; H, 7·0; N, 4·5; MeO, 9·4. $C_{18}H_{23}O_5N$ requires C, 64·8; H, 7·0; N, 4·2; MeO, 9·3%). This substance is easily soluble in water to strongly alkaline solutions but, when pure, it is not very hygroscopic; it is sparingly soluble in ether and benzene and in cold anhydrous methyl or ethyl alcohol. The base does not exhibit many of the colour reactions characteristic of codeine; with Froehde's reagent, it yields a yellow solution which becomes brown on warming, and with Mandelin's reagent it gives a brown solution which on gently warming becomes light green. Unlike codeine, it is only slowly attacked by potassium permanganate in dilute aqueous solution. The salts of this base, including the methiodide, were not obtained in a crystalline condition. As the substance has the same state of oxidation as codeinone and thebaine, a specimen was submitted to the action of hydrochloric acid under the conditions which are employed for the preparation of thebenine from thebaine, but no change occurred. The low yield of the trihydroxy-base is probably due to side reactions, further oxidation and possibly the production of stereoisomerides.

The *triacetyl* derivative is characteristic and may be most conveniently obtained from the material (A) mentioned above. 3 G. of this, heated with acetic anhydride (30 c.c.) for 75 minutes on the steam-bath, gave a brown solution which was decomposed with water, rendered alkaline by ammonia and extracted with chloroform. After removal of the solvent the residue was dissolved in methyl alcohol (10 c.c.) and the crystals which separated on cooling were collected (0·3 g.) and recrystallised from methyl alcohol in colourless plates, m. p. 200° (Found in material dried at 100° over phosphoric anhydride in a vacuum: C, 62·9; H, 6·6; N, 3·3. $C_{24}H_{29}O_8N$ requires C, 62·7; H, 6·4; N, 3·1% and $C_{22}H_{27}O_7N$ requires C, 63·3; H, 6·5; N, 3·4%). As the analytical results were in approximate agreement with the theoretical requirements of the formulæ of both the diacetyl and the triacetyl derivative of the parent base, it was vitally important to estimate the acetyl groups directly. We are greatly indebted to Professor K. Freudenberg and Dr. E. Weber, who have kindly carried out the estimations by a new micro-analytical method (Freudenberg, *Annalen*, 1923, **433**, 230; Freudenberg and Weber, *Z. angew. Chem.*, 1925, **38**, 280) [Found: $CH_3{\cdot}CO$, 27·93, 27·78, 27·87. $C_{18}H_{20}O_5N(CO{\cdot}CH_3)_3$

requires $CH_3{\cdot}CO$, 28·09%]. The acetyl groups were somewhat resistant to hydrolysis, and two distillations were necessary; the standard process gave $CH_3{\cdot}CO$, 24·6%. This might suggest that one of the acetyl groups is attached to nitrogen, were it not for the fact that the substance is a strong base readily soluble even in dilute acetic acid. A compound identical with the above-described derivative was obtained by acetylation of pure dihydroxydihydrocodeine.

Triacetyldihydroxydihydrocodeine is sparingly soluble in water and in cold methyl alcohol; its *perchlorate* crystallises from water in slender, colourless needles, m. p. 281° with slight previous decomposition.

We are indebted to the Department of Scientific and Industrial Research for grants which have enabled one of us to take part in this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, March 5th*, 1926.]

CXXVII.—*Researches on Residual Affinity and Co-ordination. Part XXVI. A Quadridentate Group in Combination with Bivalent Metals.*

By GILBERT T. MORGAN and J. D. MAIN SMITH.

IN the preceding communication of this series we showed that ethylenediaminobisacetylacetone, first prepared by Combes, furnishes a bivalent quadridentate radical which is capable of behaving as a fourfold associating group in co-ordination compounds of the metals. This fact was demonstrated by a study of the co-ordination compounds of bivalent and tervalent cobalt and the investigation has now been extended to the corresponding derivatives of bivalent copper, nickel, and palladium.

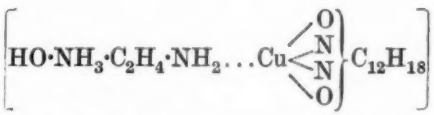
Cupric ethylenediaminobisacetylacetone, prepared originally by Combes (*Compt. rend.*, 1889, **108**, 1252), is a well-defined, highly crystalline, dark violet derivative behaving as a non-ionised complex containing one bivalent copper atom in combination with one molecular proportion of the bivalent quadridentate radical. Its constitution may be expressed by formula (I), in which the quadri-

(I.) $\left[Cu\begin{matrix}O\\N\\N\\O\end{matrix}\right\}C_{12}H_{18}\right]$ $\left[H_2O\ldots Cu\begin{matrix}O\\N\\N\\O\end{matrix}\right\}C_{12}H_{18}\right]$ (II.)

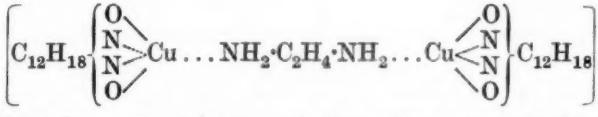
dentate radical is grouped round the metallic atom either tetrahedrally or at four points in one plane. It is, however, not possible

to decide between these possibilities, because in either case the co-ordination complex is unsaturated and readily takes up another associating unit as when the anhydrous violet copper compound absorbs water to pass into its dark green monohydrate (II).

Other addenda can be added in a similar manner to the unsaturated complex, for when Combes's violet compound is dissolved in ethylenediamine hydrate, combination occurs with one molecular proportion of the solvent, giving rise to an analogue (III) of the foregoing aquo-derivative (II).

(III.) 

This ethylenediaminehydrato-compound, when exposed in a desiccator over solid caustic soda or calcium chloride, loses all its water and half of its ethylenediamine, giving rise to the anhydrous ethylenediamine derivative (IV), in which two molecular proportions of Combes's compound are associated with one molecule of ethylenediamine.

(IV.) 

It is evident from the existence of these three compounds (II, III, and IV) that one characteristic co-ordination number of copper is 5. This conclusion is borne out by the preparation of a stable light green mono-quinoline derivative of copper acetylacetone, $[Cu(C_5H_7O_2)_2,C_9H_7N]$ (V). Similar compounds are obtainable from ammonia and pyridine, but the derivatives of these more volatile bases are unstable, losing their addenda rapidly at the ordinary temperature.

Co-ordination Numbers of Bivalent Copper.

The literature of copper compounds exhibiting residual affinity is very extensive and furnishes many diverse examples of addenda in these copper derivatives varying in number from 1 to 6, with indications of even higher values. Among the lower values, 2 and 3 stand out prominently and are represented by compounds sufficiently stable and well-defined to warrant the belief that there are copper complexes corresponding with co-ordination numbers 2 and 3. There are also numerous and varied examples among copper compounds of the higher even co-ordination numbers 4 and 6.

The results obtained in this investigation with regard to the formation of complexes with co-ordination number 5 warrant a

reconsideration of the constitutions often accepted for such substances as the following: $CuCl_2,4NH_3,H_2O$; $CuBr_2,5NH_3$; $CuSO_4,5H_2O$; $CuSO_4,4NH_3,H_2O$; $CuSO_4,5NH_3$ and $CuSO_4,5NH_2{\cdot}OH$.

In formulating these copper salts as co-ordination compounds, at least two alternative views present themselves. The associating units may be grouped exclusively round the metallic atom, giving rise to complex cations of the general type $[Cu5X]^{\cdot\cdot}$ or contrariwise one or more molecules of the various addenda may be wholly or partly associated with the anions, which thus become hydrated or ammoniated. If the latter condition could be demonstrated in any of these instances, then the co-ordination number for copper would, in such cases, become less than 5.

There are, however, other less equivocal examples of five associating units round copper in which the metallic atom is no longer in a cation but in an anion such as in pentachlorocupric acid, $H_3[CuCl_5]$ (G. Naumann, *Monatsh.*, 1894, **15**, 489) and in the double nitrites $K_3[Cu(NO_2)_5]$ and $Rb_3[Cu(NO_2)_5]$ (Kurtenacker, *Z. anorg. Chem.*, 1913, **82**, 204) and $Tl_3[Cu(NO_2)_5]$ (Cuttica and Paciello, *Gazzetta*, 1922, **52**, i, 141).

Further evidence on this type of copper co-ordination is now under investigation, particularly in regard to complexes derived from cupric iodide. These results, which indicate a descent from 6 to 5 in the number of associating units round bivalent copper, will shortly be submitted.

Electronic Structure of the Bivalent Copper Atom.

The foregoing evidence, which points to 5 as a characteristic co-ordination number for bivalent copper, has been shown by one of us (J. D. M. S.) to be a consequence of the electronic distribution in atoms first propounded two years ago (Main Smith, *J. Soc. Chem. Ind.*, 1924, **43**, 323). According to this general scheme, which was then applied to all elements, the probable structure of the bivalent cupric ion was shown to be 2, 224, 22445, 000, using ciphers to indicate the vacant sub-groups to be filled by electrons derived from associating units.

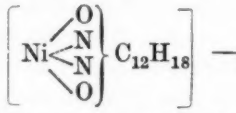
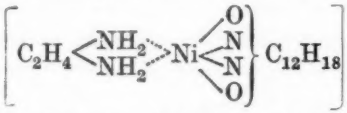
Then if, in combination with a quadridentate group, each associating atom of the group contributes two electrons to the three empty electronic sub-groups of the cupric ion, the electronic structure of the co-ordinated atom will be 2, 224, 22445, 224. This arrangement differs from the electronic structure 2, 224, 22446, 224 for the atom of krypton, the inert gas next higher than copper in atomic number, only in a shortage of one electron in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated cupric atom with co-ordination

number 4. If this incomplete 9th sub-group could be completed by the addition of a single electron (Main Smith, *J. Soc. Chem. Ind.*, 1925, **44**, 944) from the fifth associating unit of a copper co-ordination compound, then the cupric atom of co-ordination number 5 would possess the electronic structure 2, 224, 22446, 224, identical with that of the inert gas krypton.

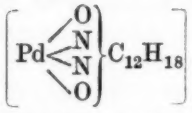
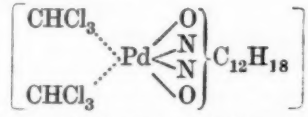
Co-ordination Numbers of Bivalent Nickel and Palladium.

The bivalent quadridentate group from ethylenediaminobisacetylacetone also furnishes well-defined, stable derivatives of bivalent nickel and palladium.

Nickel ethylenediaminobisacetylacetone (VI), which melts and even boils without decomposition providing that air is excluded, resembles Combes's copper derivative and is an unsaturated substance forming additive compounds with two molecular proportions of ammonia or with one of ethylenediamine. The latter combination is the more stable of the two, its constitution being indicated by formula (VII).

(VI.)  (VII.) 

Palladous ethylenediaminobisacetylacetone (VIII) is a fairly stable, non-ionised complex insoluble in water but dissolving in the ordinary organic solvents. From these media it separates with addenda of crystallisation. The dichloroformo-derivative, for example (IX), contains two molecular proportions of solvent.

(VIII.)  (IX.) 

The foregoing results indicate that nickel and palladium have a co-ordination number 4 in their combinations with the bivalent quadridentate group, but these compounds are unsaturated and take up addenda, suggesting that bivalent nickel and palladium have also the higher co-ordination number 6, displayed, however, in less stable derivatives.

Electronic Structures of the Bivalent Nickel and Palladium Atoms.

Nickel and bivalent palladium have yielded simple derivatives with ethylenediaminobisacetylacetone, in which the co-ordination number 4 is apparent as in Combes's simple cupric compound, and they further resemble the latter also in being co-ordinatively unsaturated, yielding addition compounds with various addenda, such as ammonia, ethylenediamine, and chloroform.

According to the general scheme of atomic structure above mentioned, the bivalent nickel atom has the probable electronic structure 2, 224, 22444, 000. If the quadridentate group, as with copper, adds four pairs of electrons to the three empty sub-groups, the electronic structure for the co-ordinated nickel atom will be 2, 224, 22444, 224. This differs from the electronic structure for the atom of the inert gas, krypton, only in a shortage of two electrons in the 9th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated nickel atom with co-ordination number 4.

The electronic structure of the bivalent palladium atom in the above scheme is 2, 224, 22446, 22444, 000, resembling that of the nickel atom with the interpolation of five sub-groups 22446. If the quadridentate group as before adds four pairs of electrons to the three empty sub-groups, the electronic structure for the palladous atom becomes 2, 224, 22446, 22444, 224. This differs from the structure of the inert gas, xenon, 2, 224, 22446, 22446, 224, only in a shortage of two electrons in the 14th sub-group, and this unsaturated arrangement may be accepted as the electronic structure for the co-ordinated palladous atom with co-ordination number 4.

Both nickel and palladous atoms in combination with the quadridentate group, however, yield addition compounds with two molecules or equivalents of ammonia, chloroform, and anhydrous ethylenediamine, and thus differ from the cupric compounds, which yield addition compounds with only one molecule or equivalent of the addenda. As in the case of copper, the addenda for nickel and bivalent palladium atoms may be regarded as due to the intervention of only one electron per bond, for the addenda are even more feebly attached to the metallic atom than in the case of copper. This conclusion is supported by the very numerous cases of organic and inorganic stable nickel compounds having the co-ordination number 4, which yield much less stable addition compounds having the co-ordination number 6. Typical examples are found in nickel acetylacetone, $Ni\{(OCMe)_2CH\}_2$, and nickel tetrammines, $Ni(NH_3)_4X_2$, which yield much less stable addition compounds with two molecules or equivalents of water, ammonia or ethylenediamine. If, as suggested, the addenda are held by bonds of only one electron as in the case of copper, the addenda add only two electrons to the 9th sub-group of the nickel structure and two electrons to the 14th sub-group of the palladous structure, thus yielding atomic structures identical in electronic arrangement with those of the inert gases, krypton and xenon, respectively.

These considerations give powerful mutual support to the view that the characteristic co-ordination number is 5 for the cupric

atom, and 6 for the nickel and palladous atoms, and to the above-mentioned scheme of distribution of electrons in atoms and in particular to the electronic structures assigned to the atoms of copper, nickel, and palladium.

Constitution of Ethylenediamine Hydrate.

It may be inferred from the knowledge that the co-ordination number of the cupric atom is 5 in addition compounds of cupric complexes with a quadridentate group, that the ethylenediamine hydrate addition compound herein described has the constitution $ecCuNH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3{\cdot}OH$, the ethylenediamine hydrate molecule not being a chelate group and being attached to the cupric atom by only one nitrogen atom, and the molecule of water being in consequence necessarily combined with the other nitrogen atom. This view is supported by the fact that on dehydration a compound of chelate ethylenediamine and the cupric atom with the co-ordination number 6 is not obtained. The product contains per cupric atom only half a molecule of ethylenediamine, which is thus still not a chelate group but has the two nitrogen atoms combined with separate cupric atoms having the co-ordination number 5. This product is obtained only by the loss of water and ethylenediamine hydrate simultaneously from two molecules of the original compound, thus indicating that the water molecule of the original compound is not in combination with the cupric atom and is firmly attached to only one nitrogen atom.

Ethylenediamine hydrate is an exceedingly stable substance and is a base nearly as strong as the alkalis, indicating that it has the constitution of an ammonium hydroxide, $(C_2H_4N_2H_5)OH$. As ethylenediamine does not give rise to basic salts containing only one molecule of acid per molecule of base, it follows that the two basic ammino-groups are completely equivalent, and that separation of the water molecule can only be effected by acids on condition that both ammino-groups react simultaneously. The two ammino-groups consequently must equally share the single hydrogen atom ionised from the hydroxyl group of the hydrate, thus leading to the constitution $[C_2H_4(NH_2)_2H]OH$. The graphic formula for ethylenediamine hydrate should thus be written :

$$\left[\begin{matrix} CH_2{-}NH_2 \\ | \\ CH_2{-}NH_2 \end{matrix}\!\!>\!H\right]OH$$

being a five-membered cyclic structure containing a hydrogen atom with co-ordination number 2.

This formulation is in complete harmony with the known properties of ethylenediamine hydrate and other polymethylenediamine

hydrates, and with the foregoing considerations relating to the ethylenediamine addition compounds of the cupric atom.

Experimental.

$C_2H_4[N{:}C(CH_3){\cdot}CH{:}C(CH_3){\cdot}O-]_2$ = ec (dibasic acid radical of ethylenediaminobisacetylacetone).*

1. *Copper Series.*

Aquo-cupric Ethylenediaminobisacetylacetone, H_2O Cuec.—On adding a solution of ethylenediaminobisacetylacetone to an aqueous ammoniacal solution of any cupric salt, glistening, bright violet scales of Combes's anhydrous cupric ethylenediaminobisacetylacetone, Cu ec, are immediately and quantitatively precipitated, but when left in contact with the mother-liquor or on exposure of the damp salt to moist air, the violet scales are wholly transformed into transparent scales varying from sage to dark green in colour. This green salt is the monohydrate of Combes's salt and is the sole product formed when the purple solution of Combes's salt in acetone is poured into dilute aqueous ammonia solution. When the pale blue cupric salt of acetylacetone undergoes prolonged treatment with aqueous ethylenediamine, a simple ethylenediammino-addition compound is not formed, although the copper salt dissolves to an indigo-blue solution. From this solution the green hydrate of Combes's salt alone separates, the ethylenediamine undergoing organic condensation with two molecules of acetylacetone, the aminated dienolic diketone being formed in combination with the cupric atom by elimination of water (Found: N, 9·2; Cu, 21·0; loss at 100°, 6·0. $C_{12}H_{20}O_3N_2Cu$ requires N, 9·2; Cu, 21·0; H_2O, 5·9%).

Aquo-cupric ethylenediaminobisacetylacetone, forming large, black tablets, dark green by transmitted light, is insoluble in water, dissolves in nearly all organic solvents to form purple solutions of the anhydrous salt, and becomes anhydrous at 100°, but is unaffected by dry or moist air at the ordinary temperature. It melts at the temperature of the anhydrous salt, 137°, to a purple liquid, and, out of contact with air, boils at a high temperature without decomposition. The vapour in contact with air deposits a copper mirror on heated glass surfaces.

Cupric Ethylenediaminobisacetylacetone Ethylenediamine Hydrate, $ecCuNH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3{\cdot}OH$.—A hot solution of Combes's anhydrous cupric ethylenediaminobisacetylacetone in ethylenediamine hydrate, on cooling, deposits large, grass-green plates of a new salt in which

* For certain details of preliminary work on the metallic derivatives of this quadridentate group we are indebted to Dr. H. D. K. Drew.—G. T. M.

one molecule of the cupric salt is combined with one molecule of the ethylenediamine hydrate (Found: Cu, 17·6, 17·4. $C_{14}H_{28}O_3N_4Cu$ requires Cu, 17·5%).

Cupric ethylenediaminobisacetylacetone ethylenediamine hydrate crystallises from ethylenediamine hydrate in large, grass-green or ivy-green plates, which are slowly decomposed on exposure to air, emitting white fumes of ethylenediamine hydrate and yielding Combes's violet salt. It dissolves to a purple solution in hot benzene, but is reprecipitated unchanged on addition of a mixture of ethylenediamine hydrate and light petroleum, in which it is insoluble. It loses all its water and half of its ethylenediamine on exposure over solid sodium hydroxide, and is converted into a new salt, sage green in colour.

Ethylenediammino-dicupric Bisethylenediaminobisacetylacetone, $C_2H_4(NH_2Cu\,ec)_2$.—On exposure of the foregoing bright green addition compound of Combes's violet salt and ethylenediamine hydrate in a confined space over solid caustic soda or fused calcium chloride, fumes of ethylenediamine hydrate are continuously emitted and a green salt is produced in which two molecules of Combes's salt are combined with one molecule of anhydrous ethylenediamine (Found: N, 13·0; Cu, 19·7. $C_{26}H_{44}O_4N_6Cu_2$ requires N, 13·3; Cu, 20·2%).

Ethylenediammino-dicupric bisethylenediaminobisacetylacetone forms glistening, sage-green scales which are stable in a confined space but are slowly decomposed on exposure to air with the formation of Combes's violet salt; it is insoluble in water and in 2*N*-caustic soda solution, but is slowly decomposed to form Combes's violet salt, and is thus distinguished from the foregoing hydrated salt, which is not decomposed by 2*N*-caustic soda solution and is only very slowly decomposed by water.

Quinolino-cupric Acetylacetone (V).—Pale blue cupric acetylacetone was dissolved in boiling quinoline, forming a dark green solution, from which, on cooling, large, sage-green plates separated. These were removed and dried in air (Found: Cu, 15·9. $C_{19}H_{21}O_4NCu$ requires Cu, 16·3%). This quinoline addition compound is stable in dry air, but is slowly decomposed by moist air and by water, or by solution in organic solvents, quinoline being lost and the simple cupric salt regenerated.

Cupric acetylacetone forms similar sage-green addition compounds with ammonia and with pyridine on addition of an alcoholic solution of the salt to a concentrated aqueous solution of the base, but these more volatile bases are rapidly lost on removal from the precipitating medium and consequently these addition compounds cannot be dried for analysis.

2. *Nickel Series.*

Nickel Ethylenediaminobisacetylacetone, Ni ec.—Hexa-aquo-nickel chloride (2·4 g. = 1 mol.) was dissolved in water (20 c.c.) and mixed with ethylenediaminobisacetylacetone (2·2 g. = 1 mol.) in alcoholic solution (29 c.c.), forming a dark reddish-brown liquid, to which was added 5*N*-sodium hydroxide solution (4 c.c. = 2 mols.). An olive-green precipitate separated, which dissolved to a reddish-black solution on heating on the steam-bath, large, brilliant bronze-red, rhomboidal, transparent scales and plates rapidly separating, which were washed with water, recrystallised from alcohol and air-dried (Found: Ni, 20·8. $C_{12}H_{18}O_2N_2Ni$ requires Ni, 20·9%).

Nickel ethylenediaminobisacetylacetone, crystallising in bronze-red scales or plates or reddish-black tablets, is insoluble in water, readily soluble in most organic solvents to red solutions, and soluble in mineral acids only with decomposition, forming acetylacetone and nickel and ethylenediamine salts. It melts at 200° to a black liquid, and, out of contact with air, boils without decomposition at a temperature approaching a red heat, forming a heavy yellow vapour, which condenses in bright red needles. The vapour, in contact with air, deposits a glistening nickel mirror on a heated glass surface, similar to the cobalt mirror obtained by heating the corresponding cobaltous salt.

Ethylenediammino-nickel Ethylenediaminobisacetylacetone, $C_2H_4(NH_2)_2Ni$ ec.—The foregoing nickel salt was dissolved in the minimum quantity of boiling ethylenediamine hydrate, forming a brownish-red solution, from which, on rapid cooling, elongated, brownish-red needles separated. These were removed, washed with light petroleum and dried over solid caustic soda (Found: Ni, 17·2 $C_{14}H_{26}O_2N_4Ni$ requires Ni, 17·2%).

The acicular form of ethylenediammino-nickel ethylenediaminobisacetylacetone slowly loses ethylenediamine on exposure; it is insoluble in water and decomposed by this medium, forming the foregoing simple salt and a strongly alkaline solution of ethylenediamine.

Diammino-nickel Ethylenediaminobisacetylacetone, $(NH_3)_2Ni$ ec.—On pouring a saturated solution of the simple nickel salt in alcohol into 18*N*-ammonia solution, brilliant red prisms separated. On drying, these rapidly lost ammonia, even over sodium hydroxide and ammonium carbonate. Analysis was possible only of the partly deamminated salt, the highest percentage of ammonia found being 7·9. The diammine requires 10·8 and the monammine 5·7%, indicating that the product was almost certainly the diammino-nickel salt.

3. *Palladous Series.*

Palladous Ethylenediaminobisacetylacetone. Pd ec.—Palladous chloride (0·9 g. = 1 mol.) was dissolved in boiling 10*N*-hydrochloric acid, and the solution rather more than neutralised with sodium carbonate. Ethylenediaminobisacetylacetone (1·2 g. = 1 mol). and 5*N*-sodium hydroxide solution (2 c.c. = 2 mols.) were then added. On heating on the steam-bath, the yellow mixture assumed a brownish-black colour. After cooling, the liquid was filtered, and the solid residue extracted with acetone until the extracts were colourless. On concentrating the orange-coloured acetone extracts, yellow prisms separated, which were recrystallised from benzene and air-dried (Found : N, 8·3; Pd, 32·4. $C_{12}H_{18}O_2N_2Pd$ requires N, 8·5; Pd, 32·5%).

Palladous ethylenediaminobisacetylacetone forms canary-yellow needles, m. p. 228°. It is insoluble in water, sparingly soluble in light petroleum, and freely soluble in most other organic solvents, from which it separates in pale yellow prisms with solvent of crystallisation, readily lost on exposure, yielding the simple salt.

Dichloroformo-palladous Ethylenediaminobisacetylacetone, $(CHCl_3)_2Pd$ ec.—From a saturated solution of palladous ethylenediaminobisacetylacetone in chloroform, large, elongated, hexagonal, pale yellow tablets separated, which were removed and dried by a very short exposure to air (Found : loss at 100°, 41·7. $C_{14}H_{20}O_2N_2Cl_6Pd$ requires $CHCl_3$, 42·1%). The addition compound, on exposure to air, only slowly loses chloroform (identified by odour), but is rapidly converted into the simple salt by heating for about an hour at 100°.

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EDGBASTON. [*Received, February 8th,* 1926.]

CXXVIII.—*Derivatives of 2-Keto-1 : 2-dihydrobenz*iso*thiazole.**

By ERNEST WILSON MCCLELLAND and ALBAN JAMES GAIT.

IT has been suggested (McClelland and Longwell, J., 1923, **123**, 3310) that the first stage in the production of the disulphide (I) from 2-dithiobenzoyl and a primary amine is the formation of

* Named " 2-thiobenzimide " in previous papers.

hydrogen sulphide and a ketodihydrobenz*iso*thiazole (II). It was pointed out that these benz*iso*thiazoles, if formed, would be

(I.) $\left[C_6H_4<\begin{matrix}S-\\CO\cdot NHR\end{matrix}\right]_2$ $C_6H_4<\begin{matrix}S\\CO\end{matrix}>NR$ (II.)

very easily reduced to the corresponding disulphides and that the failure to isolate them was probably due to their reduction by the hydrogen sulphide.

Such compounds appear to be unknown and the present investigation was undertaken with the object of synthesising them and examining their stability towards hydrogen sulphide.

Attempts to prepare 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*thiazole by the intramolecular condensation of (I; R = Ph), which in the presence of sulphuric acid might be expected to react as the sulphenic acid, $NHPh\cdot CO\cdot C_6H_4\cdot S\cdot OH$ (compare Prescott and Smiles, J., 1911, **99**, 640), were unsuccessful. According to patent literature (D.R.P.-anm. F. 35230), 2 : 2′-dithiobenzoic acid on treatment with chlorine yields a sulphur chloride, $CO_2H\cdot C_6H_4\cdot SCl$. It was therefore to be expected that 2 : 2′-dithiobenzoyl chloride would also yield a sulphur chloride (III) and that this dichloride would condense with primary amines to give the required *N*-substituted ketodihydrobenz*iso*thiazoles (II) thus:

$$\left[C_6H_4<\begin{matrix}S-\\COCl\end{matrix}\right]_2 \xrightarrow{Cl_2} \underset{\text{(III.)}}{C_6H_4<\begin{matrix}SCl\\COCl\end{matrix}} \xrightarrow{NH_2R} \underset{\text{(II.)}}{C_6H_4<\begin{matrix}S-\\CO\end{matrix}>NR}$$

2 : 2′-Dithiobenzoyl chloride, suspended in carbon tetrachloride, dissolved on treatment with dry chlorine, presumably owing to the formation of the dichloride (III). This chlorinated solution reacted with aqueous ammonia to give 2-keto-1 : 2-dihydrobenz*iso*thiazole. In a similar way the chlorinated solution reacted with aniline, *o*-toluidine, and aqueous methylamine to give compounds of the type (II) in which R is Ph, *o*-C_6H_4Me, and Me, respectively. On oxidation with hydrogen peroxide these compounds were converted into the corresponding "saccharins." The interaction of the chlorinated solution of 2 : 2′-dithiobenzoyl chloride with *n*-propylamine yielded an oily substance which was undoubtedly 2-*keto*-1-n-*propyl*-1 : 2-*dihydrobenzisothiazole*, as on oxidation it was converted into N-n-*propyl*-o-*benzoicsulphinide*.

The 1-*phenyl*, 1-o-*tolyl*, and 1-*methyl* derivatives of 2-keto-1 : 2-dihydrobenz*iso*thiazole in alcoholic solution are rapidly reduced by hydrogen sulphide with deposition of sulphur and formation of disulphides identical with the products obtained by the action of the corresponding amines on 2-dithiobenzoyl. The afore-mentioned suggestion of McClelland and Longwell hereby receives strong

confirmation. 2-Keto-1 : 2-dihydrobenz*iso*thiazole also is reduced by hydrogen sulphide. The fact that it can be isolated by the action of ammonia on 2-dithiobenzoyl may be due to its being slightly more stable than its derivatives towards hydrogen sulphide, as previously suggested.

Selenium analogues of 2-keto-1 : 2-dihydrobenz*iso*thiazole and certain of its derivatives have been prepared by an analogous method (Lesser and Weiss, *Ber.*, 1924, **57**, 1077).

EXPERIMENTAL.

2 : 2′-Dithiobenzoyl chloride was prepared by the action of phosphorus pentachloride on 2 : 2′-dithiobenzoic acid (*Ber.*, 1898, **31**, 1670) and was crystallised from benzene before use in the following experiments.

The derivatives of 2-keto-1 : 2-dihydrobenz*iso*thiazole described below were prepared by the following general method. Dry chlorine was bubbled through a suspension of 2 : 2′-dithiobenzoyl chloride (5 g.) in carbon tetrachloride (40 c.c.; dried over calcium chloride) until solution was complete. The excess of chlorine having been removed by a current of dry air, the solution was added slowly, with vigorous stirring, to aqueous ammonia (40 c.c.; *d* 0·880), 30% aqueous methylamine (excess), or the amine (aniline, 8 g.; *o*-toluidine, 10 g.) diluted with carbon tetrachloride. During the addition the aqueous ammonia and the solutions of the amines were cooled in ice. The product of the reaction was either precipitated or obtained by evaporation of the dried carbon tetrachloride solution.

2-*Keto*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = H) was precipitated on addition of the chlorinated solution of 2 : 2′-dithiobenzoyl chloride to the aqueous ammonia and was crystallised from methyl alcohol and finally from water (yield 80%). It melted at 155—156°, alone or mixed with a specimen prepared by the action of ammonia on 2-dithiobenzoyl.

2-*Keto*-1-*phenyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = Ph). — In this preparation aniline hydrochloride was precipitated; it was filtered off and the carbon tetrachloride allowed to evaporate at room temperature. The residual solid crystallised from methyl alcohol in fine, colourless needles, m. p. 140° (Found: C, 68·4; H, 4·1; S, 13·9. $C_{13}H_9ONS$ requires C, 68·7; H, 4·0; S, 14·1%).

2-*Keto*-1-*o*-*tolyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = *o*-C_6H_4Me) was obtained as a brown oil which slowly solidified; after crystallisation from methyl alcohol it melted at 122—123° (Found: C, 69·7; H, 4·5; S, 13·4. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·5; S, 13·3%).

2-*Keto*-1-*methyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = CH_3) was

obtained from the carbon tetrachloride after separation from the aqueous solution, as a brown oil which slowly solidified; it crystallised from benzene–light petroleum in fine, colourless needles, m. p. 51—52° (Found: C, 58·0; H, 4·3; S, 19·5. C_8H_7ONS requires C, 58·1; H, 4·3; S, 19·4%).

This *iso*thiazole is sparingly soluble in ether and light petroleum and very soluble in alcohol or benzene. On treatment with hydrochloric acid the crude oil obtained above yielded a *hydrochloride*, which was readily hydrolysed by water but crystallised from hydrochloric acid in colourless needles, m. p. 124—127°. The hydrochloride appears to be unstable, as varying results were obtained in the estimation of the chlorine and its melting point gradually fell on keeping in a vacuum desiccator.

N-n-*Propyl*-o-*benzoicsulphinide*, $C_6H_4<\begin{matrix}SO_2\\CO\end{matrix}>N\cdot C_3H_7$.—A chlorinated solution of 2 : 2′-dithiobenzoyl chloride, prepared by the general method, was added to an excess of propylamine diluted with carbon tetrachloride. The solid material was filtered off, and the carbon tetrachloride evaporated. The oil thus obtained was oxidised in glacial acetic acid with hydrogen peroxide (30%). The product crystallised from water in fine, colourless needles, m. p. 73—75° (Found: S, 14·1; N, 6·1. $C_{10}H_{11}O_3NS$ requires S, 14·2; N, 6·2%).

Oxidation of the Benzisothiazoles.—A solution of 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*thiazole (0·2 g.) in glacial acetic acid was heated with 30% hydrogen peroxide (1 c.c.) for 1 hour at 100°. On cooling, a white, crystalline product was obtained. This, after recrystallisation from glacial acetic acid, melted at 189—190°, and at 189° when mixed with authentic *N*-phenyl-*o*-benzoicsulphinide, m. p. 190·5° (*Amer. Chem. J.*, 1895, **17**, 320).

In a similar way 2-keto-1-*o*-tolyl-1 : 2-dihydrobenz*iso*thiazole yielded a substance, m. p. 171—173° (*N*-*o*-tolyl-*o*-benzoicsulphinide has m. p. 172—175°; *loc. cit.*, p. 327).

2-Keto-1-methyl-1 : 2-dihydrobenz*iso*thiazole (the crude oil) was instantly converted by cold hydrogen peroxide (30%) into a white, crystalline substance. This, after recrystallisation from glacial acetic acid and finally from methyl alcohol, melted at 129—130°, alone or mixed with *N*-methyl-*o*-benzoicsulphinide.

Reduction of the Benzisothiazoles.—Hydrogen sulphide was bubbled slowly through a solution of 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*thiazole in ethyl alcohol at 50°. In a few minutes a precipitate of sulphur appeared; the current of gas was then stopped, and the solution filtered as quickly as possible. The filtrate slowly deposited colourless needles contaminated with sulphur. After several crystallisations from glacial acetic acid, the product was obtained free from

sulphur; it melted at 236—238°, and at 237° when mixed with 2 : 2′-dithiobenzophenylamide (m. p. 239°), prepared by the action of aniline on 2-dithiobenzoyl.

2-Keto-1-*o*-tolyl-1 : 2-dihydrobenz*iso*thiazole, reduced in a similar way, gave a product which after recrystallisation from methyl alcohol melted at 219—220°, alone or mixed with the product obtained by the action of *o*-toluidine on 2-dithiobenzoyl.

The reduction of 2-keto-1-methyl-1 : 2-dihydrobenz*iso*thiazole by hydrogen sulphide, under the same conditions, yielded a substance which after crystallisation from glacial acetic acid and methyl alcohol melted at 220—221°, alone or mixed with 2 : 2′dithiobenzomethylamide, prepared by the action of methylamine on 2-dithiobenzoyl.

The authors desire to express their thanks to Professor Smiles for the interest he has taken in this work and for his helpful suggestions.

KING'S COLLEGE, LONDON. [*Received, January 28th,* 1926.]

CXXIX.—*The Vapour Pressures of Chlorine Dioxide.*

By FREDERICK ERNEST KING and JAMES RIDDICK PARTINGTON.

A CONNECTED series of measurements of the vapour pressures of chlorine dioxide from the melting point to the boiling point of the substance does not appear to have been recorded. A few isolated measurements, in poor agreement, are given in the literature. Millon (*Ann. Chim. Phys.*, 1843, **7**, 314; *Annalen*, 1843, **46**, 281) gives + 20° or +32° as the boiling point, but does not describe the method used. He correctly states that chlorine dioxide attacks mercury, and dissolves in concentrated sulphuric acid to a bright yellow solution, but his assertion that the latter decomposes at 10° with evolution of chlorine, oxygen, chlorine dioxide, and "chlorine trioxide" we do not confirm. Millon also correctly described the colour of liquid chlorine dioxide as red, "like the brightly-coloured sulphur chloride," *i.e.*, the monochloride containing excess of chlorine, but he overestimated the explosive properties of the liquid. Brandau (*Annalen*, 1869, **151**, 340) gives the boiling point of what he calls chlorine trioxide as 8—9° at 745 mm.: the substance must have been the dioxide. Pebal (*ibid.*, 1875, **177**, 1) determined the boiling point by a rather crude method as 8·7° at 725·7 mm. Schacherl (*ibid.*, 1881, **206**, 68) attempted to determine the vapour pressure by means of a mercury manometer in direct communication with a water manometer, the metal being protected from the gas

by a long column of water. Schacherl first noticed that liquid chlorine dioxide, although exploding violently when the process is initiated, is not liable to spontaneous, erratic detonation, as asserted by Millon, provided that all traces of organic matter are excluded and the substance is manipulated entirely in glass. Schacherl gives the following pressures, which are really those over a saturated solution, although he remarks that the yellow colour of the solution had not passed round the water limb of the manometer before the conclusion of the measurements.

$t°$	10·6	7·6	9·6	14·0	14·1	16·9	10·3	7·6
p (mm.)	767·8	728·8	784·4	961·9	983·9	1162·7	1335·6	1329·1

It is quite clear, as Schacherl himself admits, that these values are completely vitiated by decomposition of the gas at the higher temperatures, and that the first value only can be taken into account. He concluded that the vapour-pressure method must be abandoned as unsuitable for the determination of the boiling point. This was really an incorrect conclusion, since, if he had taken care not to raise the temperature too far above the boiling point, there would probably have been very little decomposition. Schacherl then made a direct estimation of the boiling point with a mercury thermometer bulb immersed in the liquid contained in a small open bulb in a water-bath. The temperature rose slowly to 9·9°, remained constant for a short time, then varied between 9·9° and 10·1°, then returned to 9·9°, and remained constant until practically all the liquid had evaporated. The pressure was 730·9 mm. The liquid, it was found, could be boiled rapidly at + 30° without explosion, and the vapour recondensed by cooling at 8·9°. During the boiling-point determination, care was taken to avoid superheating, and the liquid during the whole series of measurements boiled steadily without bumping.

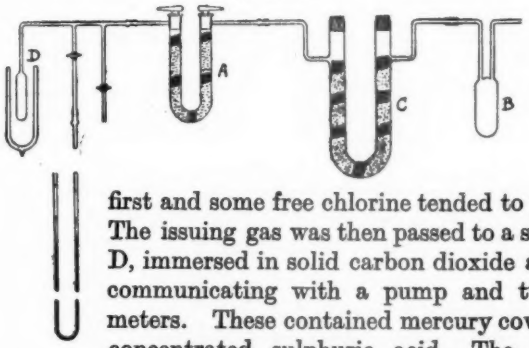
Experimental.

The chlorine dioxide was prepared by a method stated by Spring (*Bull. Acad. roy. Belg.*, 1875, **39**, 882) to yield chlorine trioxide, a substance up to the present unknown. The method involved the action of chlorine on dry silver chlorate. We have convinced ourselves that the only gaseous products of this reaction are chlorine dioxide and oxygen, so that it probably proceeds according to the equation $2AgClO_3 + Cl_2 = 2AgCl + 2ClO_2 + O_2$. The chlorine dioxide is easily liquefied out of the gas by cooling and can be obtained pure and dry.*

* Garzarolli Thurnlackh (*Annalen*, 1881, **209**, 184) refers to Spring's work at the end of his paper and suggests that the gas may have been a mixture of the composition $Cl_2O + 4ClO_2$ rather than Cl_2O_3. He promised to investigate the matter further, but does not appear to have done so.

According to Spring, the reaction begins in the cold, but we have found that it is quite inappreciable below about 80° and occurs regularly and smoothly at about 90°. The silver chlorate was prepared from chloric acid and silver oxide, dried in a desiccator over phosphorus pentoxide, and then about 10 g. were filled into a U-tube with ground stopcocks (A, Fig. 1), with alternate plugs of dry glass wool. Ramsay lubricant proved to be efficient for the ground joints and stopcocks; it was only very slightly attacked, if at all, during the few hours necessary for actual measurements. Pure dry chlorine, liberated by warming liquid chlorine (from potassium permanganate and hydrochloric acid) in a bulb, B, and dried by passing over phosphorus pentoxide in the tube C, was passed slowly over the chlorate, the tube A being maintained at 85—95° in an electrically heated air-bath. With fresh chlorate, the reaction was slow at

FIG. 1.



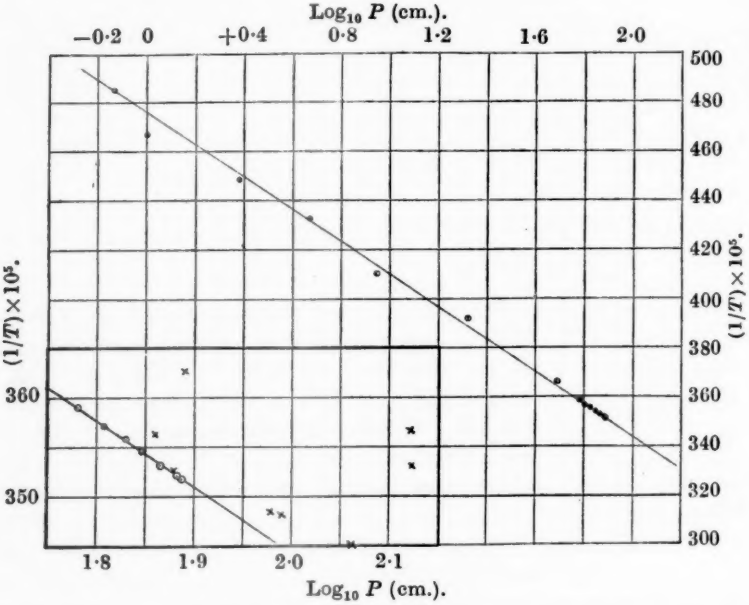
first and some free chlorine tended to pass over. The issuing gas was then passed to a small bulb, D, immersed in solid carbon dioxide and ether, communicating with a pump and two manometers. These contained mercury covered with concentrated sulphuric acid. The first (not shown) served to indicate the pressure after exhaustion and during filling; the second, which was closed by a tap until the actual measurements were begun, served to measure the pressures. By working in this way, excessive attack of the mercury surface used for measurement was avoided. The columns of acid were of the same length in each limb so as to compensate each other. We satisfied ourselves that, although mercury is attacked with the deposition of a white powder, no permanent gas is evolved from the sulphuric acid, which slowly becomes bright yellow in colour. The oxygen accumulating was removed from time to time by pumping.

The chlorine dioxide condensed in the bulb as a crystalline solid of the colour of potassium dichromate. If any excess of chlorine had passed through, this either floated unchanged on the surface of the solid dioxide or condensed along with dioxide to a deep red liquid which did not solidify in the freezing mixture. In either case, the chlorine was easily removed by pumping for a few minutes with

the bulb immersed in the freezing mixture. The pressure finally fell suddenly and the red crystals remained. The vapour pressure of the solid at −80° was negligible.

By adding ether to the freezing mixture until all the solid carbon dioxide had disappeared, it was possible to raise the temperature slowly in steps to −30°. Melting occurred sharply at −59°, both solid and liquid being at first present, and all the solid melted at this temperature. This result is in agreement with the only previous observation, that of Faraday (*Phil. Trans.*, 1845, **135**, 155), who found the melting point −59°.*

FIG. 2.



By further addition of ether, the temperature was gradually raised, the temperatures being measured on a pentane thermometer. After −30°, a mixture of ice and salt, pure ice, and water were used successively, with a mercury thermometer.

The gauge pressures were subtracted from the mercury column reading corresponding with the vacuum attained in the apparatus before admitting gas. After the measurements, the chlorine dioxide was resolidified by immersing the bulb in solid carbon dioxide and

* Faraday's result is given in most works of reference as −76°; this, however, is the temperature on the Fahrenheit scale used by Faraday. The correct figure is given in Watts' Dictionary, 1890, vol. 2, p. 13.

ether, and the original vacuum recovered, showing that decomposition had not occurred during the measurements.

The logarithms of the pressures recorded in Table I are plotted against the reciprocals of the absolute temperatures in Fig. 2, and it will be seen that a fair approach to a straight line is obtained. The part near the boiling point is drawn on an enlarged scale to the left. It so happened that the barometric pressure corresponded exactly with 760 mm. when the boiling point was reached, so that the value of the latter, 11·0°, could be determined directly.

The isolated points observed by Pebal and Schacherl are also shown. The first measurement of the latter in the vapour pressure series, when corrected for the vapour pressure of water at 15°, lies almost on the curve, but the remaining measurements show great irregularity. The direct measurement of the boiling point made by Schacherl, *viz.*, 9·9°/730·9 mm., also lies on the curve.

TABLE I.

T ° Abs.	193	206	214*	223	232·5	243·5	255	273
p mm. obs. ...	‡	7	10	24	47	88	201	490
T ° Abs.	278·3	279·9	281	282	283	284†	284·2	
p mm. obs. ...	608	642	674	700	732	760	769	

* Melting point. † Boiling point. ‡ Not measurable.

From the values of the vapour pressures at different temperatures, it is possible to calculate the latent heat of evaporation of liquid chlorine dioxide by means of the formula :

$$\lambda = 4{\cdot}576\{\log(p_2/p_1)\}T_1T_2/(T_2 - T_1) \text{ cal. per mol.}$$

From data near the boiling point the value 6520 is obtained. From this, by division by the absolute boiling point T_0, we find the Trouton coefficient λ/T_0 of 23. The values of this calculated by the two formulæ of Nernst are :

$$8{\cdot}5 \log T_0 = 20{\cdot}85 \text{ and } 9{\cdot}5 \log T_0 - 0{\cdot}007T_0 = 21{\cdot}3,$$

and from Wartenberg's formula $7{\cdot}4 \log T_0 + 1{\cdot}985 = 20{\cdot}2$.

The ratio of the absolute temperatures corresponding with vapour pressures of 760 mm. and 200 mm. (really 201 mm.) is 1·114, which is the value shown by Ramsay and Young to correspond with normal liquids (*Z. physikal. Chem.*, 1887, **1**, 249). These considerations seem to point to very little, if any, association of chlorine dioxide in the liquid state, so that its formula in both the gaseous and the liquid state may be considered to be ClO_2. The colours of the solid, liquid, and gaseous forms would also point to the same conclusion.

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CXXX.—*The Oxidation Potential of the System Selenium Dioxide–Selenium.*

By SYDNEY RAYMOND CARTER, JOHN A. V. BUTLER, and FRANK JAMES.

SELENIUM dioxide is readily reduced to selenium and it appeared that a study of the oxidation potential of the system selenium dioxide–selenium would furnish interesting data for comparison with that of the analogue: sulphur dioxide–sulphur (Carter and James, J., 1924, **125**, 2231).

Preliminary *E.M.F.* measurements were carried out with various half-elements in combination with the calomel electrode. Each cell contained several platinum foil electrodes, some of which were plain and others platinised. The solid selenium used in cells 2, 3 and 5 was the red amorphous variety. In some cases, the platinum foil was buried in the selenium, whilst in others the selenium was deposited electrolytically.

Cell 1.	(Pt)|0·1*M*-SeO_2,	0·1 *M*-Na_2SeO_4,	H_2O
2.	(Pt)|0·1*M*-SeO_2,	Se (solid),	H_2O
3.	(Pt)|0·1*M*-SeO_2,	Se (solid),	10*N*-HCl
4.	(Pt)|0·1*M*-SeO_2,	Se (in solution),	10*N*-HCl
5.	(Pt)|Se (solid),	10*N*-HCl	

1 and 2 gave ill-defined potentials and they were greatly affected by polarisation. 3 and 4 gave well-defined potentials. In 5, the potential was ill-defined, but on the addition of selenium dioxide it rose several tenths of a volt and became steady.

From these and subsequent experiments it was concluded that a definite potential was exhibited, provided that the solution were strongly acid and that selenium dioxide and selenium were each present in solution. In the case of the selenium, it might be present in quantity to form either a saturated or an unsaturated solution. In this connexion, the solubility of selenium is important and experiment revealed the following facts:

1. Red amorphous selenium was stirred with concentrated hydrochloric acid at 20° for 3 days, but no selenium was dissolved. Moreover, under these conditions no selenium dioxide was formed, although the solution was in contact with air.

2. Selenium is soluble in concentrated hydrochloric acid in presence of selenium dioxide. The solubility of selenium in 0·1*M*-SeO_2 and 11·6*N*-HCl is 1·35 g. per litre (within 5%).

3. The solubility of selenium falls off rapidly with diminishing concentration of acid, and, on dilution of saturated solutions with water, the red amorphous selenium is precipitated.

It was therefore decided to determine the oxidation potential of the system selenium–selenium dioxide–concentrated hydrochloric acid, and to study the influence of changes in concentration of (*a*) selenium, (*b*) selenium dioxide.

In order to obtain reproducible values of the *E.M.F.* it was obvious that the quantity of dissolved selenium would have to be carefully controlled.

Materials. — Selenium dioxide was prepared by dissolving amorphous selenium (B.D.H.) in concentrated nitric acid and evaporating the solution to dryness. The product was twice sublimed in small quantities in a large crucible and thereby freed from tellurium. Pure amorphous selenium was prepared from the purified selenium dioxide by passing sulphur dioxide through a slightly acid solution; after thorough washing on an asbestos pad, the precipitate was dried in a vacuum. The hydrochloric acid employed throughout was B.D.H., As.T. quality.

Preparation of Solutions.—A solution of selenium in concentrated hydrochloric acid containing selenium dioxide was prepared by shaking amorphous selenium with the liquid for several days. The clear solution (deep amber colour) was withdrawn into a pipette through a pad of glass wool and portions were analysed. The stock solution had the following composition: 0·066*N*-SeO_2, 0·0134*N*-Se, 11·6*N*-HCl. This was used for making up the cell solutions by suitable dilution with hydrochloric acid of the same concentration and addition of the proper amounts of selenium dioxide either as the solid or from the stock solution. The composition of some of the solutions was checked by analysis.

Analysis.—The determination of selenium dioxide was based on that of Norris and Fay (Gooch, "Methods in Chemical Analysis," 1912, p. 383) for acid solutions. 10 C.c. of the concentrated acid solution are added to 300 c.c. of ice and water. 50 C.c. of *N*/10-sodium thiosulphate are then run in, the excess being titrated with standard iodine solution, starch paste being used as indicator. This method gave accurate results if the conditions were strictly observed.

The estimation of the amount of dissolved selenium was a more difficult matter. At first, the greater part of the hydrochloric acid was evaporated on the water-bath, and the selenium precipitated by the addition of water. This method gave variable results owing apparently to the volatilisation of a portion of the selenium. The method finally adopted was to dilute 100 c.c. of the solution with a litre of water. The selenium separated in a very finely-divided form which did not settle readily. On adding a few c.c. of a strong solution of potassium chloride, however, the precipitate rapidly

settled in a compact curdy form, which was filtered off through a Gooch crucible, dried at 110°, and weighed. Long heating at this temperature caused no loss of weight by volatilisation. The filtrate showed no sign of containing any free selenium. It was colourless and clear, and no perceptible turbidity appeared on further dilution.

Hydrochloric acid was determined in a separate portion by suitable dilution and titration with standard sodium carbonate.

Electrical Measurements.—It was feared that the presence of concentrated hydrochloric acid in one half of the cell would give rise to a troublesome liquid boundary and make accurate measurements impossible.

The following type of cell was finally found to be most suitable for the purpose:

$$(\mathrm{Pt})\,\underset{11{\cdot}6\ N\text{-HCl}}{|yN\text{-}SeO_2 + zN\text{-Se}}\,\underset{\text{Stationary junction.}}{|N\text{-HCl}}\,\underset{\text{Flowing junction.}}{|KCl\ (\text{sat.})}\,\underset{KCl\ (\text{sat.})}{|Hg_2Cl_2}\,|\mathrm{Hg}$$

This arrangement gave reproducible results and was not liable to fluctuations of more than a few tenths of a millivolt during the experiments. Moreover the boundary potentials are of types which may be evaluated if required.

A stationary junction being used at the *N*-HCl|KCl (sat.) boundary, variations of 0·0025 volt over a 10-minute range were experienced, whilst, with the flowing junction, readings constant to 0·0001 volt during 15 minutes were obtained. This is of interest, since the flowing junction has hitherto been applied to junctions of the type HCl|KCl for concentrations of 0·1*N* and *N* (Lamb and Larson, *J. Amer. Chem. Soc.*, 1920, **42**, 229). The present work shows how it may be employed advantageously in connecting a saturated potassium chloride solution with highly concentrated acid.

The electrodes were of platinum platinised in the usual way. A fresh electrode took some time to acquire a definite potential, but electrodes that had been immersed in one of the solutions, after being washed once or twice with a fresh solution, rapidly assumed a steady potential. In some preliminary experiments a metre bridge in conjunction with a capillary electrometer was employed. With this arrangement, it was found that the electrodes, particularly in the more dilute solutions, were very readily polarised, even with the small currents which passed in finding the balance point, and took some time to recover the original potential. In the later work a Cambridge ionisation potentiometer was used, giving readings direct to 0·2 millivolt with a sensitive A. M. galvanometer. No

trouble was experienced with this arrangement on account of polarisation.

Three electrodes were placed in the electrode vessel. After use in a few cells an electrode often became irregular and differed from the other two. Fairly frequent replatinising was necessary. The electrode vessel was kept in a thermostat at $20° \pm 0{\cdot}1°$ during the measurements. The saturated calomel electrode was one of a battery of four which were frequently compared and at no time differed by more than 0·25 millivolt. The calomel electrodes were at room temperature. This was determined exactly by a thermometer in the liquid of one of them, at the time of every measurement, and the correction introduced.

Reproducibility and Constancy.—Although with the more concentrated solutions the mean potentials were easily reproduced to within a fraction of a millivolt (*e.g.*, cell D), minor fluctuations, usually less than a millivolt, were sometimes observed. On the other hand, the solutions containing the more minute concentrations of selenium exhibited a gradual drift in the potential. This was most apparent in cell C, where a gradual decrease from 0·5452 to 0·5247 volt at 12° over a period of 22 hours was observed. This was not due to changes in the immediate vicinity of the electrodes, for only a minute alteration of the potential occurred on shaking the cell. The drift appeared to be due to some decomposition in the cell, which was accelerated by the higher temperature of the thermostat, this being slightly above that of the room. A portion of the solution C, which had remained at room temperature for 24 hours, gave a slightly lower potential than the original reading; when placed in the electrode vessel in the thermostat, its rate of drift was greater. It appeared that the reaction concerned was the reduction of selenium dioxide by hydrochloric acid: $SeO_2 + 4HCl = Se + 2H_2O + 2Cl_2$.

The formation of selenium to only a slight extent in this reaction would have an appreciable effect on the selenium concentration at the minute concentrations of the more dilute cells. This supposition was supported by the fact that a stock solution of selenium dioxide in concentrated hydrochloric acid, kept at room temperature, acquired after some days a faint yellow tint. The potential of a platinum electrode in this solution measured against the saturated calomel electrode was 0·614 volt, which would correspond to a selenium concentration of about $10^{-5}M$.

Measurements.—A typical set of potentiometer readings is in Table I, which gives the observations for three freshly prepared cells, D1, D2 and D3, respectively. (The selenium electrode is positive with respect to the calomel.)

E ($t°$) is the observed $E.M.F.$ when the oxidation cell is at 20° and the calomel electrode is at room temperature, $t°$: E (20°) is the $E.M.F.$ after correcting the calomel electrode to 20°.

TABLE I.

$[SeO_2] = 0{\cdot}0866$, $[Se] = 0{\cdot}00134$, $[HCl] = 11{\cdot}6$.

Cell.	Hrs.	Mins.	$E(t°)$ observed.			$E(t°)$ mean.	E (20°).
D. 1.		10	0·5738	0·5739	0·5736	0·5733 $t = 13{\cdot}5°$	0·5720
	1	20	0·5732	0·5732	0·5730		
	3	20	0·5729	(0·5716)	0·5728		
D. 2.		10	0·5733	0·5733		0·5734 $t = 13{\cdot}0°$	0·5720
		40	0·5742	0·5743			
	1	5	0·5728	0·5728			
	3	5	0·5718	0·5718			
	20	0	0·5678	0·5678			
D. 3.	0	40	0·5734	0·5735		0·5729 $t = 14{\cdot}5°$	0·5718
	1	35	0·5726	0·5726			
	2	30	0·5726	0·5726			
	5	40	0·5708	0·5708			

Similar determinations were made with solutions of different concentrations and the results are in Table II.

TABLE II.

$[HCl] = 11{\cdot}6N$.

Cell.	$[SeO_2]$.	[Se].	E (20°).	ΔE.
A_1	0·087	0·0134	+0·5501	—
A_2	0·087	0·0134	0·5498	0·0222
D	0·087	0·00134	0·5720	
E	0·087	0·000134	0·5970	0·0250
B	0·0087	0·00134	0·5460	
F	0·0087	0·000134	0·5720	0·0260
C	0·00087	0·000134	0·5436	—

In Cell A_1, the junction N-HCl|KCl (sat.) is stationary, but in A_2 and all the other cells the flowing junction was used.

The Influence of Concentration of Selenium Dioxide and of Selenium on Oxidation Potential.

(*a*) *Selenium.*—Table II gives this relation, since in Cells A_2, D and E the $[SeO_2] = 0{\cdot}087$ is constant and [Se] undergoes tenfold changes. Cells B and F afford a similar comparison. ΔE is the difference in $E.M.F.$ for a tenfold change in [Se] and it amounts to 0·0222 to 0·0260 volt.

(*b*) *Selenium Dioxide.*—Table III gives this relation similarly, and it will be seen that ΔE for a tenfold change in $[SeO_2]$ varies from 0·0250 to 0·0284 volt.

TABLE III.

Cell.	$[SeO_2]$.	[Se].	E (20°).	ΔE.
D	0·087	0·00134	0·5720	0·0260
B	0·0087	0·00134	0·5460	
E	0·087	0·000134	0·5970	0·0250
F	0·0087	0·000134	0·5720	
C	0·00087	0·000134	0·5436	0·0284

Mechanism of the Oxidising Action of Selenium Dioxide and of Sulphur Dioxide.

The reduction of selenium dioxide in concentrated acid solution may conceivably proceed in a number of ways, of which the following may be considered.

1. The selenium dioxide dissolves in concentrated acid to form selenium tetrachloride, which ionises into quadrivalent selenium ions, $Se^{\cdot\cdot\cdot\cdot}$. On reduction, the four positive changes are removed and elementary selenium results:

$$SeO_2 + 4HCl \rightleftharpoons SeCl_4 + 2H_2O \rightleftharpoons Se^{\cdot\cdot\cdot\cdot} + 4Cl' + 2H_2O \rightleftharpoons Se + 4Cl' + 2H_2O + 4\oplus.$$

The potential variations, ΔE, would be given by $\Delta E = 0{\cdot}058/4 \,.\, \log [Se]/[SeO_2]$, and for a tenfold change in [Se] or in $[SeO_2]$, $\Delta E = 0{\cdot}058/4 = 0{\cdot}0145$ volt.

2. The reduction does not proceed entirely from the quadrivalent state down to elementary selenium, but only through certain intermediate stages, for example, from quadrivalent to bivalent selenium. The essential portion of such a process may be represented

$$Se^{\cdot\cdot\cdot\cdot} = Se^{\cdot\cdot} + 2\oplus,$$

whence $\Delta E = 0{\cdot}058/2 \,.\, \log [Se^{\cdot\cdot}]/[Se^{\cdot\cdot\cdot\cdot}] = 0{\cdot}058/2 \,.\, \log [Se]/[SeO_2]$, and for a tenfold change in [Se] or in $[SeO_2]$, $\Delta E = 0{\cdot}058/2 = 0{\cdot}029$ volt.

Since part of the selenium dioxide is used in dissolving the selenium, the effective concentration is actually less than $[SeO_2]$ and a value somewhat smaller than 0·029 for ΔE will be obtained.

The existence of derivatives of bivalent selenium is indicated by the solubility of selenium in strong acid solutions containing selenium dioxide: $SeO_2 + Se = 2SeO$. In this connexion, it may be observed that selenium dissolves in selenic acid giving a green solution believed to contain Se_2O_3, an analogue of $SeSO_3$ which is formed by dissolving selenium in sulphuric acid (*Chem. News*, 1889, **59**, 268).

Either hypothesis depends on certain assumptions regarding the degree of ionisation and the unimolecular nature of the respective constituents in the equations. Experiments on these points are still proceeding. The experimental results for ΔE fall between those demanded by the two theories, but are rather in favour of the second.

The hypothesis that selenium acquires positive charges and behaves as an electropositive element is reasonable, since it has certain characteristics of a metal which are exhibited by its analogue tellurium, although scarcely at all by sulphur. Nevertheless the

analogy with sulphur, even if only shown to a slight extent, is of interest in a study of the oxidising properties of sulphur dioxide and would furnish an explanation if sulphur could also become electropositive in acid solution (J., 1920, **117**, 1246).

Since negatively charged selenium ions Se'' or Se_n'' have already been identified in alkaline solutions, the present indication of positively charged selenium ions in acid solution furnishes additional evidence of the amphoteric nature of selenium (compare Le Blanc, Reichenstein, Müller, and Abegg; references, *Z. physikal. Chem.*, 1921, **97**, 257; 1922, **100**, 346).

The Effect of Light.—The potential of one of the oxidation cells, which had been kept in darkness, was not affected by sudden exposure to direct sunlight, or to the light of four filament lamps at a distance of a foot. On the other hand, bright metallic electrodes (made by melting selenium on platinum) in hydrochloric acid solutions of selenium dioxide and selenium gave a potential which was distinctly influenced by exposure to light. The selenium rapidly lost its brightness and the photosensitiveness disappeared. A selenium electrode made by the cathodic deposition of selenium on a selenium rod, and therefore covered with a layer of the amorphous kind, was quite unaffected by light.*

The photosensitiveness of the *E.M.F.* of selenium in aqueous solutions has been observed by Sabine and others (for references see C. Ries, "Das Selen," 1918, p. 188) and, although the significance of the presence of concentrated acid, selenium dioxide and dissolved selenium in determining the potential has not hitherto been emphasised, it is obviously of value in explaining the processes underlying many of their experiments.

These considerations are also useful in explaining the electrometric titration of selenium solutions by the bimetallic electrode system of Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 933).

Summary.

The system selenium dioxide–selenium in concentrated hydrochloric acid gives a reproducible oxidation potential which has been measured.

The potential is unaffected by the action of light.

The influence of concentration of selenium and of selenium dioxide on potential has been studied, the changes for tenfold dilutions corresponding to 0·022—0·028 volt.

The oxidising action of selenium dioxide is provisionally attributed

* We are indebted to Mr. W. F. Waters for some assistance in these experiments.

to the presence of selenium tetrachloride, which yields positively charged selenium ions.

The oxidising action of selenium dioxide and of its analogue, sulphur dioxide, are compared.

We desire to express our thanks to the Department of Scientific and Industrial Research for a grant which enabled one of us (F. J.) to take part in this investigation.

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CXXXI.—*Applications of Thallium Compounds in Organic Chemistry. Part III. Alkylations.*

By CHRISTINA MARY FEAR and ROBERT CHARLES MENZIES.

THE preparation of alkyl derivatives by heating organic thallous compounds with alkyl iodides, suggested by the resemblance between thallous and silver halides, proceeds smoothly if the thallous compound is soluble in the alkylating agent, or if, being of an amorphous nature, it presents to it a large surface, whilst sparingly soluble, well-crystallised substances enter into the reaction slowly, if at all.

Thallous palmitate, for instance, which is appreciably soluble in methyl iodide, is completely converted into methyl palmitate by boiling with this solvent for 4 hours. Again the thallous salt of ethyl acetoacetate, readily soluble in cold ethyl iodide, requires 3 hours for ethylation, and the amorphous yellow *trithallium methylglucoside*, insoluble in methyl iodide, gives, after treatment for 5 hours, a trimethyl methylglucoside in good yield. On the other hand, treatment of the well-crystallised, sparingly soluble tetrathallium tartrate with boiling methyl iodide for 100 hours gives an incompletely methylated product, whilst an attempt to methylate the thallous salt of *o*-nitrophenol had to be discontinued. The preparation of trimethyl methylglucoside from trithallium methylglucoside is interesting in view of McKenzie's suggestion (J., 1899, **75**, 765) that the most plausible explanation of methylation by Purdie's silver oxide method is that an intermediate unstable silver derivative is formed which subsequently undergoes double decomposition with the alkyl halides (see also Lander, J., 1900, **77**, 747; 1903, **83**, 416).

The rotations observed both in this case and in that of the product of methylation of tetrathallium tartrate indicate that at any rate in these instances racemisation does not occur.

EXPERIMENTAL.

Treatment of their thallous salts with alkyl iodides affords a useful means of preparing small quantities of the esters of higher fatty acids. Thus from 0·47 g. and 0·55 g. of thallous stearate, 0·18 g. (m. p. 38·5°; yield 62%) and 0·26 g. (m. p. 37·5°; yield 79%) of methyl stearate were obtained, respectively, after refluxing for 4 hours with methyl iodide, and recovery of excess of this solvent, by extracting the resulting mixture of methyl stearate and thallous iodide with ether (Found in the latter sample: C, 76·4; H, 12·9. Calc., C, 76·4; H, 12·8%). By using larger quantities of material and benzene as solvent, almost theoretical yields may be obtained, thus 3·24 g. (theory, 3·26 g.) of methyl stearate (m. p. 38·5°) were produced by boiling 5·33 g. of thallous stearate with methyl iodide in benzene, a quantitative yield of thallous iodide also resulting.

The smaller-scale preparations, however, illustrate a convenient technique when small quantities of the higher fatty acids are under examination, it being easy to obtain from less than 1 g. of the acid its titration value, and its ethyl or methyl ester pure and in quantity sufficient for analysis and determination of melting point. Thus 0·579 g. and 0·557 g. of palmitic acid dissolved in alcohol required respectively 7·5 c.c. and 7·0 c.c. of 0·307*N*-aqueous thallous hydroxide (calc., 7·35 c.c. and 7·0 c.c.). On evaporation of the solution resulting from the former titration and treatment of the residual dry thallous palmitate with boiling methyl iodide, 0·4 g. of methyl palmitate was obtained (yield 66%; m. p. after recrystallisation from methyl alcohol 29·5°. Found: C, 75·4; H, 13·0. Calc., C, 75·5; H, 12·7%). Evaporation to dryness before treatment with methyl iodide is essential, as, on addition of methyl iodide to the solution resulting from the second titration and boiling under reflux as before, a product was obtained which had an acid reaction and a high melting point (31·5°).

By using propyl iodide, 2 g. of *propyl palmitate* were obtained from 5 g. of thallous palmitate by boiling for 1 hour (yield 63%; m. p. 15·3—15·4°, b. p. 209°/22 mm. Found: C, 76·5; H, 12·95. $C_{19}H_{38}O_2$ requires C, 76·4; H, 12·8%). The low yield was due to loss in manipulation.

Ethylation of Ethyl Acetoacetate.—A boiling solution of 23·4 g. of thallous ethyl acetoacetate (Christie and Menzies, J., 1925, **127**, 2372) in ethyl iodide rapidly deposited thallous iodide as a brick-red powder which became yellow after 2 hours. After boiling for a further hour, it was filtered off from the cooled mixture (yield, 21·8 g.; calc., 23·3 g.). On fractionation, 8·6 g. of ethyl ethylacetoacetate (yield 77·5%) distilled between 192° and 195° (uncorr.)/

756 mm. (Found: C, 60·7; H, 9·0. Calc., C, 60·7; H, 8·9%. $D_{15°}^{15°}$ 0·9924, $n_D^{15°}$ 1·4237. R_D, 40·72. Calc. for keto-form, 40·98, for enol-form, 41·92; and for the isomeric ethyl β-ethoxycrotonate, 42·08. Compare Lander, *loc. cit.*, p. 738).

Trithallium methylglucoside may be obtained in good yield as a yellow, amorphous powder by adding methylglucoside dissolved in a little water to a hot concentrated solution of thallous hydroxide. If 4 equivalents of the latter be used to each molecular equivalent of methylglucoside, the thallium content of the product approximates closely to that required for trithallium methylglucoside (Found as iodide: Tl, 76·4, 76·15. $C_7H_{11}O_6Tl_3$ requires Tl, 76·2%). The trithallium methylglucoside used for the methylation described below was prepared from 21·6 g. of α-methylglucoside (m. p. 165·5°; $[\alpha]_D$+158·8° for a 5·2% solution in water) in 13 c.c. of water and 206 c.c. of 1·62*N*-thallous hydroxide (3 equivs.), which immediately before the addition of the methylglucoside was concentrated by boiling to about half-bulk; 76·8 g. (yield 85%) separated at once (Found as iodide: Tl, 73·8%). 36·5 G. of this product were boiled with methyl iodide for 5 hours; the reaction was then complete. The excess of methyl iodide was removed, and the residue extracted with methyl alcohol; 9·8 g. of syrup (dried in a vacuum at 100°) were obtained, the theoretical yield calculated for trimethyl methylglucoside being 10·7 g. On distillation three fractions were obtained: (1) 2·25 g., b. p. 137°/2·2 mm.; (2) 4·35 g., b. p. 136·6°/2·3 mm. to 137·2°/1·5 mm.; (3) 1 g., b. p. 140°/2·5 mm. to 164°/1·8 mm. The optical and analytical data are in the following table:

	n_D.	$[\alpha]_D$ in water.	$[\alpha]_D$ * in ethyl alcohol.	C %.	H %.	OMe %.
(1)	1·4569	164° (1·6%)	165·9° (0·8%)	50·4	8·65	50·4
(2)	1·4592	153·1° (1·2%)	154·6° (1·2%)	50·9	8·5	49·0
(3)	1·464					46·0
	Calc. for trimethyl methylglucoside:			50·8	8·5	52·5

* Compare Purdie and Bridgett, J., 1903, **83**, 1037, and Haworth, J., 1915, **107**, 13.

Attempted Preparation of Methyl Dimethoxysuccinate.—From 75 g. of tetrathallium tartrate, boiled under reflux with methyl iodide for approximately 100 hours, 12·5 g. of a syrup were obtained, which distilled as a homogeneous liquid, b. p. 146°/25 mm. to 146·1°/23 mm., n_D 1·4363, $[\alpha]_D$ 72·17° (Found: OMe, 50·8, 51·6. Calc. for four methoxy-groups, OMe, 60·2%; for three methoxy-groups, OMe, 48·4%). The syrup did not solidify and a nucleus of methyl dimethoxysuccinate, kindly supplied by Professor Haworth, was dissolved.

Preparation of o-Methoxybenzaldehyde.—From 20·2 g. of thallous

salicylaldehyde, refluxed for 50 hours with methyl iodide in benzene, after removal of unchanged thallium salicylaldehyde by agitation with aqueous sodium hydroxide and subsequent distillation in steam, 5·2 g. of *o*-methoxybenzaldehyde, m. p. 36·3° (yield 62%) were obtained (Found: OMe, 21·0. Calc., OMe, 22·8%) (compare Irvine, J., 1901, **79**, 668).

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UNIVERSITY OF BRISTOL. [*Received, February 27th*, 1926.]

CXXXII.—*Determination of the Rate of Hydrolysis of Sparingly Soluble Esters.*

By R. CHRISTIE SMITH and H. A. PATERSON.

THE rate of hydrolysis of esters is most conveniently determined by estimating the amount of free acid formed at successive intervals. With sparingly soluble esters this involves the use either of large quantities of ester solutions, or of smaller quantities, giving relatively larger percentage errors. The use of strong acid (or base) for hydrolysis in order to speed up the reaction and so give increased titrations, brings in its train the difficulty of accurately determining the amount of base (*e.g.*, baryta) necessary for neutralisation of the acid. A method has been evolved which minimises the above difficulties.

In the reaction equation $dx/dt = kC$ the velocity coefficient can be interpreted as the fraction of the concentration C which is converted in the unit of time dt, and, for our purpose, it will be sufficiently accurate to define k as the fraction of the concentration C transformed in one minute. If, therefore, the solution is kept with a constant concentration C of ester, the same amount of ester will be transformed every minute. Hence it will only be necessary to keep the solution with a constant concentration of ester during a sufficiently long period to allow of a reasonable titration being obtained. The most convenient concentration is, of course, that of saturation. Hence if x c.c. of N-baryta represent the amount of ester transformed per minute in a 25 c.c. sample, the weight of ester transformed in 100 c.c. is $0{\cdot}004\,Mx$ g.

In order to test the accuracy with which k could be determined by this method, propyl acetate, ethyl propionate, and propyl butyrate (see Table I), whose velocity coefficients could also be

determined in the usual way, were chosen. The results do not show such good agreement in the case of propyl acetate as of propyl butyrate, but this is ascribed to the fact that propyl acetate is more soluble, and hence diluted the aqueous layer to an abnormal extent (see below).

TABLE I.

Ester.	k (homogeneous method).	k (heterogeneous method).
Propyl acetate .	0·0063	0·0061
Ethyl propionate	0·0068	0·0071
Propyl butyrate.	0·0039	0·0039

TABLE II.

Ester.	k (by new method).	Solubility (g. per 100 c.c.).
Benzyl acetate .	0·0051	0·234
Benzyl propionate	0·0056	0·078
Phenyl acetate .	0·0046	0·588

The velocity coefficients for the homogeneous reaction were determined in the usual manner. For the heterogeneous reaction of the substances in Table I, 250 c.c. of N-hydrochloric acid were shaken with an excess of the ester in a 300 c.c. ground-stoppered bottle in a rotary thermostat at 25°. At intervals, 25 c.c. of solution were withdrawn, 25 c.c. of N-sodium hydroxide added, and the excess of acid was titrated with baryta, the amount of ester transformed per minute being calculated from the titre. In the cases of benzyl acetate, benzyl propionate, and phenyl acetate, only 25 c.c. of N-hydrochloric acid were placed in the bottle, an excess of ester was added, and, after a given period in the thermostat, the whole was titrated. To ensure greater accuracy, the additions of normal acid and base were checked by weighing. The solubilities of these esters were determined by basic hydrolysis of 25 c.c. of saturated solution. The results are in Table II.

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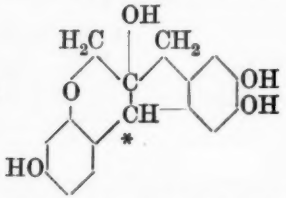
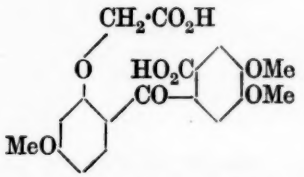
CXXXIII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part I. Veratrylidene-7-methoxychromanone and an Account of a New Synthesis of some Benzopyrylium Salts.*

By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON.

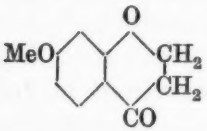
THE investigation of brazilin and hæmatoxylin by analytical methods, commenced in 1901 (Part I, Gilbody, Perkin, and Yates, J., **79**, 1401) and completed in 1909 (Part X, Perkin and Robinson, J., **95**, 381), resulted in the demonstration that brazilin has the constitution (I) and that hæmatoxylin is an analogous derivative of pyrogallol. In the course of the work a number of derivatives

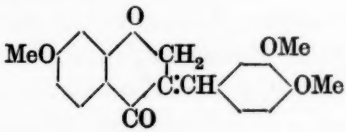
of brazilin and hæmatoxylin were synthesised, the more important being anhydrobrazilic acid, brazilinic acid, and the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids (Perkin and Robinson). Brazilinic acid (II) is an example of a derivative containing all the carbon atoms of trimethylbrazilin, and the correctness of the carbon skeleton of (I) was further confirmed by the

(I.) 

 (II.)

synthesis of *iso*brazilein and of *iso*hæmatein (Crabtree and Robinson, J., 1918, **113**, 859; 1922, **121**, 1033), substances which contain intact the ring-system of brazilin. There exists, however, no synthetical * proof of the position of the hydroxyl group in (I), since the production of 3 : 7-dihydroxychromone, an oxidation product of brazilein (Schall and Dralle, *Ber.*, 1888, **21**, 3016), could be explained in a natural manner by several brazilein formulæ and, for example, by that in which the hydroxyl is in the position denoted by an asterisk in (I). Apart from this consideration an obvious interest attaches to the synthesis of brazilin, an interest which is only heightened by the difficulty of the problem and by the probable necessity of devising new methods for its solution. In 1911, Tschitschibabin and Nikitin (*J. Russ. Phys. Chem. Soc.*, **43**, 1185) published a note on 7-methoxychromanone (III), and this led two of us to submit a preliminary note (P., 1912, **28**, 7) on the experiments which had been made on the same subject with the object of synthesising trimethylbrazilin.

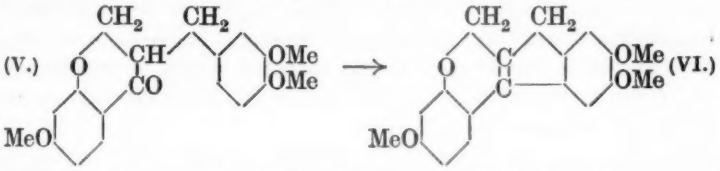
(III.) 

 (IV.)

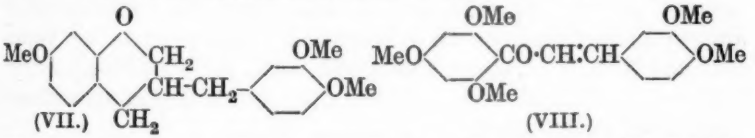
3-Veratrylidene-7-methoxychromanone (IV), m. p. 140°, was described in the note of 1912 and comment was made on its close relationship to trimethylbrazilin. Pfeiffer and Grimmer (*Ber.*, 1917, **50**, 911) then announced their intention of attacking the problem of the synthesis of brazilin and its derivatives and selected the method indicated in the above-mentioned note of 1912. These

* The position assigned to the hydroxyl in (I) is indicated by the fact that tetramethyldihydrobrazileinol yields trimethylbrazilone on oxidation (Engels, Perkin, and Robinson, J., 1908, **93**, 1130).

authors reported the preparation of anisylidene-7-methoxychromanone, and in consequence the fact that a nearer relative of brazilin, namely, veratrylidene-7-methoxychromanone, had been prepared was pointed out in a footnote to a paper in this *Journal* (1918, **113**, 859). Undeterred by this, Pfeiffer and Emmer (*Ber.*, 1920, **53**, 945) proceeded to the preparation of veratrylidene-7-methoxychromanone, m. p. 140°, and stated that they had succeeded in reducing the substance to a dihydro-derivative (V) by means of hydrogen in the presence of platinum black.



The experiments on this subject, interrupted at the time because of other interests, have now been resumed, and in this communication we bring together some observations arising out of work as yet unfinished. The preparation of (V) was one of the primary objects of the investigation, since dehydration to (VI) should be feasible. We are, however, of the opinion, for various reasons, that the product of the catalytic * hydrogenation of veratrylidene-7-methoxychromanone is 3-homoveratryl-7-methoxychroman (VII) and not the ketone (V) as suggested by Pfeiffer and Emmer (*loc. cit.*).

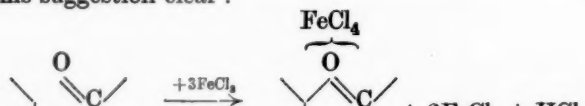


This result is by no means unique, since Freudenberg (*Ber.*, 1920, **53**, 1416) has shown that the pentamethoxychalkone (VIII) is reduced to the related diphenylpropane derivative by hydrogen in presence of spongy platinum.

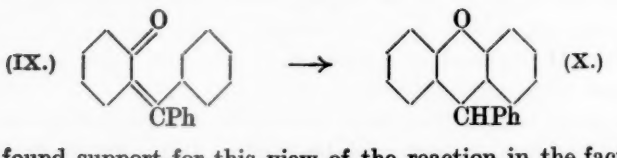
Further attempts to reduce veratrylidene-7-methoxychromanone to a dihydro-derivative will be made. Our objects in making certain further experiments are explained in the sequel (pp. 947, 948, 950). In the presence of acid condensing agents veratrylidene-7-methoxychromanone (IV) might be expected to undergo internal condensation with formation of *iso*brazilein salts, readily recognisable on account of the intense green fluorescence which they exhibit. Under several sets of conditions it was, in fact, noticed that substances exhibiting intense green fluorescence could be derived from

* We employed palladium as the catalyst, but it should be noted that platinum is usually regarded as even more efficient.

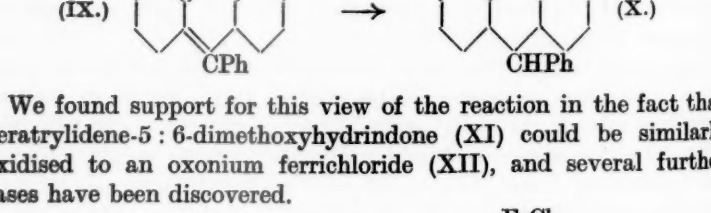
veratrylidene-7-methoxychromanone. The yield was usually very small, but when the unsaturated ketone was dissolved in acetic anhydride and anhydrous ferric chloride added, a relatively considerable amount of an oxonium ferrichloride was produced. The new salt was readily purified and exhibited an even more striking fluorescence than *iso*brazilein chloride trimethyl ether. It has the composition $C_{19}H_{15}O_5Cl_4Fe$ and is therefore derived from veratrylidenemethoxychromanone, $C_{19}H_{16}O_5$, by some process of oxidation. In considering this matter it seemed possible that the pyrylium ring, which the salt obviously contained, might be produced, not by modification of the heterocyclic system already present, but by attachment of the oxygen of the carbonyl group to carbon of the veratrole nucleus. The following partial formulæ will serve to make this suggestion clear:



Such a reaction, leading to the formation of a benzopyrylium salt, has not been previously observed, but it is similar, both in principle and in method, to Dilthey's synthesis of pyrylium salts (*J. pr. Chem.*, 1916, **94**, 53) and it also resembles many methods of preparation of oxazine, thiazine and azine dyestuffs. The simplest analogy is furnished by an observation recently made by Gomberg and Nishida (*J. Amer. Chem. Soc.*, 1923, **45**, 190): *o*-hydroxytriphenylcarbinol in solution above 100° yields 9-phenylxanthane (X), no doubt through the intermediate (IX).



We found support for this view of the reaction in the fact that veratrylidene-5 : 6-dimethoxyhydrindone (XI) could be similarly oxidised to an oxonium ferrichloride (XII), and several further cases have been discovered.



The process is nevertheless not a very general one and up to the present we have only found it to succeed with the veratrylidene, *o*-veratrylidene or piperonylidene derivatives of cyclic ketones. Thus veratrylideneacetoveratrone and *m*- or *p*-methoxybenzylidene-5 : 6-dimethoxyhydrindone gave negative results.

Experimental.

m-*Methoxyphenol.*—The conditions for the semi-methylation of resorcinol have been studied and the following process has been devised. Potassium hydroxide (40 g.) dissolved in water (100 c.c.) was gradually added to a mixture of resorcinol (110 g.), alcohol (100 c.c.), and methyl sulphate (120 c.c.), which was frequently shaken and cooled in running water. An hour afterwards, an equal quantity of aqueous potassium hydroxide was gradually introduced and finally the mixture was heated on the steam-bath for 45 minutes. The solution was then acidified, extracted with benzene and the separated benzene layer was washed with aqueous sodium hydroxide until nothing more was removed. The alkaline solutions were acidified and again extracted with benzene. This process removes unchanged resorcinol and resorcinol dimethyl ether may be recovered from the first benzene solution. The second benzene extract was dried and distilled, 50 g., b. p. 240—242°, being obtained.

β-m-*Methoxyphenoxypropionic Acid.*—This substance was originally obtained from *m*-methoxyphenol in aqueous alkaline solution by interaction with β-iodopropionic acid. The use of β-bromopropionic acid results in rather improved yields, but β-chloropropionic acid is still better. A solution of β-chloropropionic acid (60 g.) in water (225 c.c.) and sodium bicarbonate (45·3 g.) was mixed with one of *m*-methoxyphenol (67·5 g.) in aqueous potassium hydroxide (100 c.c. of 30%), and the liquid heated on the steam-bath for 3 hours. After acidification, the mixture was extracted with ether, and the acid removed from the extract by means of aqueous sodium bicarbonate. β-*m*-Methoxyphenoxypropionic acid (30 g.) and recovered *m*-methoxyphenol (28—30g.) were ultimately isolated.

We refrain from detailed descriptions of the substances mentioned in the note of 1912 (*loc cit.*), the properties of which have since been placed on record by Pfeiffer and his colleagues.

m-β-Hydroxyethoxyanisole, b. p. 290°/15 mm., was prepared from *m*-methoxyphenol, sodium ethoxide, and ethylene chlorohydrin in alcoholic solution. In an attempt to replace the hydroxyl group in this substance by bromine with the ultimate object of preparing β-*m*-methoxyphenoxypropionitrile, a curious result was

obtained. The glycol ether (11 g.) was dissolved in benzene and phosphorus tribromide (20 g.) added, causing a copious evolution of hydrogen bromide. The mixture was gently heated in the steam-bath for 2 hours, and the neutral product isolated. This was dissolved in alcohol, and the solution boiled for 3 hours after the introduction of a concentrated aqueous solution of potassium cyanide (5 g.). On addition of water, a solid (6 g.) was precipitated and the substance crystallised from alcohol in long, colourless needles, m. p. 65° (Found: C, 70·1; H, 6·6. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%). The substance appears to be the ethylene ether of *m*-methoxyphenol, $MeO{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_4{\cdot}OMe$.

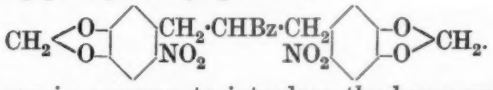
7-*Methoxychromanone* (III) has been prepared by several methods but, although it is not satisfactory, the original process of dehydration of methoxyphenoxypropionic acid in benzene solution by means of phosphoric anhydride is still the best. Phosphoric anhydride (80—90 g.) was gradually added to a gently boiling solution of methoxyphenoxypropionic acid (30 g.) in benzene (200 c.c.). After heating for 4 hours, the neutral ketone was isolated and purified by distillation. The yield was 6—8 g., b. p. 197°/30 mm., m. p. 56° after crystallisation from light petroleum. The semicarbazone separates from alcohol in glistening plates, m. p. 222° (decomp.).

3-*Veratrylidene*-7-*methoxychromanone* (IV).—This substance was at first prepared by condensation of 7-methoxychromanone and veratraldehyde in methyl-alcoholic solution in presence of potassium hydroxide, but the following is a much improved method. A rapid stream of hydrogen chloride was passed for one hour through a solution of methoxychromanone (5 g.) and veratraldehyde (5 g.) in acetic acid (10 c.c.) cooled in a freezing mixture. Next day the deep red solution was filled with a red crystalline mass of the *hydrochloride* of the unsaturated ketone and this was collected and decomposed with crushed ice. The substance was finally crystallised from much methyl alcohol, separating in colourless needles, m. p. 141°. The yield was 5·6 g.

3-*Homoveratryl*-7-*methoxychroman* (VII).—A solution of veratrylidene-7-methoxychromanone (7 g.) in acetic acid (200 c.c.) was mixed with aqueous palladous chloride (30 c.c. of 1%) and agitated in an atmosphere of hydrogen until absorption of the gas slackened. The temperature was then raised to 50—60° and the agitation in hydrogen continued for about 6 hours. Most of the acetic acid was removed from the filtered solution by distillation under diminished pressure, and the residue neutralised with aqueous sodium carbonate. The colourless solid which was precipitated was collected and when once crystallised from methyl alcohol had m. p. 89°. This is the m. p. assigned by Pfeiffer and Emmer (*loc. cit.*)

to the supposed ketonic product of the catalytic hydrogenation of veratrylidenemethoxychromanone. After three or four successive crystallisations from methyl alcohol or from aqueous acetone, the substance is obtained in slender, colourless needles, m. p. 96—97° (Found: C, 72·2; H, 7·2. $C_{19}H_{22}O_4$ requires C, 72·6; H, 7·0%). The substance dissolves in sulphuric acid to a pale rose solution and is inactive towards reagents for the carbonyl group. We do not go so far as to assert that the products of the hydrogenation of veratrylidenemethoxychromanone in presence of platinum (Pfeiffer and Emmer) and of palladium are identical, although we think it probable that this will prove to be the case.* We have not been able to isolate any product of the reduction other than that here described and it is noteworthy that, whereas the semicarbazone of the reduction product of anisylidenemethoxychromanone was described (Pfeiffer and Emmer, *loc. cit.*), no proof, other than analysis, was offered of the ketonic nature of the reduction product, m. p. 89°, of veratrylidenemethoxychromanone.

Di-ω-6-nitropiperonylisobutyrophenone,



—Attempts are in progress to introduce the homoveratryl group into 7-methoxychromanone by a direct process and preliminary experiments on the interaction of the sodium derivative of acetophenone and homopiperonyl † bromide have been made. Powdered sodamide (2 g.) was added to acetophenone (6 c.c.) dissolved in dry ether (75 c.c.) and, after the mixture had been occasionally shaken during an hour, homopiperonyl bromide (11 g.) was added to the clear solution. The mixture was heated on the steam-bath for 1 hour, water was added, and ether and acetophenone were removed in

* It would be anticipated that the m. p. of a chromanone should be higher than that of the related chroman.

† Possibly on account of its close relation to piperonal the alcohol $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}OH$ has been called piperonyl alcohol, and consequently the amine, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, has been named homopiperonylamine. This nomenclature is, however, erroneous and its continuance must necessarily create confusion. The historical case for regarding the group $CH_2O_2{:}C_6H_3{\cdot}$ as piperonyl is overwhelming; thus Ladenburg termed

$$CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CHO,$$

piperonylacrolein and the words piperonyl, veratryl, and anisyl have been very widely employed to indicate the corresponding substituted phenyl groups. The compound often called piperonyl alcohol is really homopiperonyl alcohol and the base for which the usual name is homopiperonylamine is best termed β-piperonylethylamine. It is obviously undesirable to employ one and the same word to denote two different radicals (compare Robinson and Robinson, J., 1914, **105**, 1461; Oberlin, *Arch. Pharm.*, 1925, **9**, 10).

a current of steam. The residual yellow oil could not be crystallised but, on nitration in acetic acid solution, it yielded a compound which crystallised from benzene in needles, m. p. 193° with sintering at 175° (Found: C, 51·5; H, 3·5. $C_{16}H_{13}O_8N_3$ requires C, 51·2; H, 3·5%). The substance appears to be *dinitrodihomopiperonylamine*, $CH_2O_2{:}C_6H_2(NO_2)\cdot CH_2\cdot NH\cdot CH_2\cdot C_6H_2(NO_2){:}O_2CH_2$, obtained from homopiperonyl bromide and ammonia followed by nitration. The experiment was therefore repeated under the same conditions with the single exception that ammonia was removed from the ethereal solution by means of a current of nitrogen before introduction of the homopiperonyl bromide. In this case also the product was an oil which gave a nitro-derivative, crystallising from benzene in slender needles, m. p. 160—161° (Found: C, 60·4, 60·3; H, 3·9, 4·0; N, 6·0. $C_{24}H_{18}O_9N_2$ requires C, 60·3; H, 3·8; N, 5·9%). The composition of this substance is in agreement with the hypothesis that it is the ketone figured at the head of this section. We have not yet completed our experiments on the homoveratrylation of methoxychromanone, but it may be mentioned that in the course of the preparation of homoveratryl alcohol a further case of the production of a derivative of cinnamic acid in a Cannizzaro reaction, carried out in the presence of ethyl alcohol, has been observed (compare Perkin and Stoyle, J., 1923, **123**, 3174). Potassium hydroxide (30 g.) dissolved in ethyl alcohol (75 c.c. of 98%) was added to veratraldehyde (20 g.) dissolved in the same solvent (25 c.c.). Next day, the crystals which had separated were collected and found to consist of potassium 3 : 4-dimethoxycinnamate and to yield 7·8 g. of the corresponding acid. Veratric acid and homoveratryl alcohol were isolated from the filtrate in the usual manner.

2-Bromo-5 : 6-dimethoxy-1-hydrindone, $C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle CHBr$. —A portion (18 c.c.) of a solution of bromine (1 c.c.) in carbon tetrachloride (20 c.c.) was gradually added to 5 : 6-dimethoxyhydrindone (3·0 g.) dissolved in warm carbon tetrachloride (30 c.c.). After 1 hour the thick paste that had been produced (3·0 g.) was washed with carbon tetrachloride; it crystallised from alcohol in very pale yellow, rectangular plates, m. p. 157° (Found: Br, 28·3. $C_{11}H_{11}O_3Br$ requires Br, 29·5%).

2-Cyano-5 : 6-dimethoxy-1-hydrindone, $C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle CH\cdot CN$. —This substance was prepared in order to attempt the synthesis of a coumarin derivative by condensation with resorcinol. Such a substance would be closely related to trimethylbrazilin. A mixture of 2-bromo-5 : 6-dimethoxy-1-hydrindone (3 g.), alcohol (40 c.c. of 95%), potassium cyanide (1·5 g.), and water (20 c.c.) was boiled

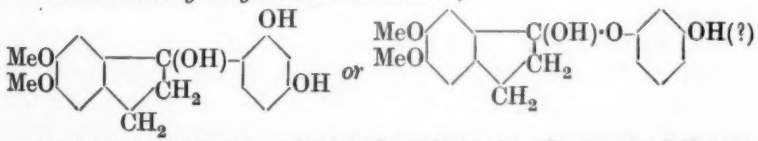
under reflux for 3 hours, then cooled, acidified with acetic acid, and extracted with ether. The residue left after removal of the solvent from the extract crystallised from alcohol in clusters of radiating needles (1—1·5 g.), m. p. 174° (Found : C, 66·1; H, 4·8. $C_{12}H_{11}O_3N$ requires C, 66·3; H, 5·0%). The substance dissolves in dilute aqueous potassium hydroxide to a very pale yellow solution and gives no coloration with alcoholic ferric chloride. On hydrolysis with boiling 50% sulphuric acid, 5 : 6-dimethoxyhydrindone, identified by conversion into its piperonylidene derivative, m. p. 245°, was obtained. In a subsequent experiment, the proportion of water employed was reduced, and in this case, in addition to the above-described nitrile, a polymeric modification or condensation product of it was obtained. Bromo-5 : 6-dimethoxyhydrindone (10 g.), absolute alcohol (60 c.c.), potassium cyanide (3·5 g.), and water (5 c.c.) were mixed and then boiled under reflux for 2 hours, water (10 c.c.) being gradually introduced during this period. The product was added to water, and the solid (5 g.) collected. On acidification the filtrate gave 1·5 g. of the normal nitrile. The main product was sparingly soluble in most organic solvents and crystallised from glacial acetic acid in needles, m. p. 256—257° to a red liquid (Found : C, 66·4; H, 5·4%). The substance is insoluble in dilute aqueous potassium hydroxide.

Ethyl 5 : 6-*Dimethoxy*-1-*hydrindone*-2-*carboxylate*,

$$C_6H_2(OMe)_2\begin{matrix}CO\\CH_2\end{matrix}>CH\cdot CO_2Et.$$

—A solution of the nitrile, m. p. 174°, described in the last section, in 20 times its weight of absolute alcohol was saturated with hydrogen chloride at the ordinary temperature for 3 hours, then boiled for 10 minutes and added to ice-cold water. The solid which separated crystallised from alcohol in colourless needles, m. p. 138° (decomp.) (Found : C, 63·9; H, 6·3. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%). This ester gives with ferric chloride in alcoholic solution a transient green and then a blue coloration. We have not yet prepared a coumarin derivative from either the nitrile or the ester by condensation with resorcinol, although a number of trials have been made.

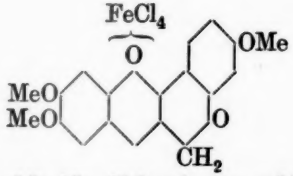
5 : 6-*Dimethoxy*-1-*hydrindone-resorcinol*,



—A solution of dimethoxyhydrindone (9·0 g.) and resorcinol (7·0 g.) in acetic acid (35 c.c.) was saturated with hydrogen chloride in the cold, kept for 1 hour, and added to water (150 c.c.). The resulting

clear liquid was neutralised with sodium carbonate; the yellow, crystalline deposit separated from boiling water in silky needles, m. p. 78° (Found: C, 67·9; H, 6·0. $C_{17}H_{18}O_5$ requires C, 67·6; H, 5·9%). A small quantity of a yellow oil was separated in the above process on account of its sparing solubility in hot water. This consists of a substance which crystallises from methyl alcohol in needles, m. p. 227°. The by-product has not yet been further examined, nor has the compound, m. p. 78°, been characterised by the preparation of derivatives. It is remarkably sensitive to alkalis, being quantitatively resolved into its components, namely, dimethoxyhydrindone and resorcinol, by means of cold aqueous sodium hydroxide. Attempts to prepare an indene derivative by dehydration of this substance were fruitless. It is not a mere molecular compound, since it is not obtained in the absence of a condensing agent.

2 : 3-[7-*Methoxychromeno* (4 : 3)]-6 : 7-*dimethoxybenzopyrylium Ferrichloride*,

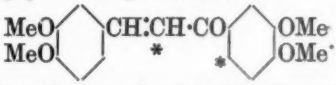


—Anhydrous ferric chloride (5·0 g.) was added to a solution of veratrylidene-7-methoxychromanone (1·0 g.) in acetic anhydride (25 c.c.) and when the reaction had subsided a further quantity of ferric chloride (3·0 g.) was added. After 10 minutes, the product was added to water (250 c.c.), and a ferrichloride precipitated by addition of a concentrated solution of ferric chloride in hydrochloric acid. The substance (yield almost quantitative) crystallised from acetic acid in crimson, prismatic needles, m. p. 213°, exhibiting a blue reflex (Found: C, 43·7, 43·4; H, 3·5, 3·2. $C_{19}H_{15}O_5Cl_4Fe$ requires C, 43·6; H, 3·3%). Solutions of this salt in all solvents and particularly those in alcohol and acetic acid exhibit an extraordinarily brilliant greenish-yellow fluorescence. The salt is very sparingly soluble in acetic acid and more readily soluble in hot formic acid.

2-m-*Methoxybenzylidene*-5 : 6-*dimethoxy*-1-*hydrindone*.—This compound was obtained by condensation of dimethoxyhydrindone and *m*-methoxybenzaldehyde in hot alcoholic solution containing a few drops of concentrated aqueous potassium hydroxide. The yield was practically quantitative and the sparingly soluble substance crystallised from ethyl acetate in pale yellow needles, m. p. 164—165° (Found: C, 73·6; H, 5·7. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

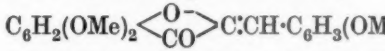
Neither this substance nor the isomeric anisylidenedimethoxyhydrindone could be converted into a pyrylium salt by means of ferric chloride in acetic anhydride solution.

3 : 4-*Dimethoxystyryl Veratryl Ketone*,

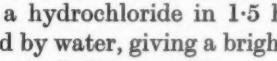


—An ethyl-alcoholic solution of equivalent quantities of veratraldehyde and acetoveratrone, together with a few drops of concentrated aqueous potassium hydroxide, was boiled for 10 minutes. The oil then precipitated by water solidified on repeated washing with cold water and aqueous alcohol. The substance crystallised from alcohol in flat, yellow prisms, m. p. 116° (Found : C, 69·3; H, 6·1. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%). The compound is not changed to a pyrylium salt by the action of ferric chloride in acetic anhydride solution. This fact may be compared with the ready conversion of veratrylidenedimethoxyhydrindone into an oxonium ferrichloride by oxidation with ferric chloride. In the latter case, the carbon atoms in the asterisked positions in the above formula are connected by a methylene group.

2-*Veratrylidene*-4 : 6-*dimethoxycoumaranone*,



—A solution of equivalent quantities of veratraldehyde and 4 : 6-dimethoxycoumaranone (Sonn, *Ber.*, 1917, **50**, 1265) in five times their weight of acetic acid was cooled in a freezing mixture and saturated with hydrogen chloride. The liquid was filled with a mass of deep red crystals of a hydrochloride in 1·5 hours; these were collected and decomposed by water, giving a bright yellow substance which crystallised from alcohol in needles, m. p. 175° (Found : C, 66·1; H, 4·9. $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·2%). No pyrylium salt could be isolated from the product of the action of ferric chloride and acetic anhydride on this substance.

2-*Veratrylidene*-1-*hydrindone*,  .—An ice-cold mixture of veratraldehyde (4·5 g.), α-hydrindone (3 g.), and acetic acid (15 c.c.) was saturated with hydrogen chloride and after 3 hours the scarlet hydrochloride was collected, washed with acetic acid, and decomposed with water; the resulting yellow compound crystallised from acetic acid in prisms, m. p. 175° (Found : C, 76·6; H, 5·8. $C_{18}H_{16}O_3$ requires C, 77·2; H, 5·7%).

2 : 3-*Indeno*(1 : 2)-6 : 7-*dimethoxybenzopyrylium Ferrichloride* (formula similar to XII).—Anhydrous ferric chloride (15 g.) was added in portions of about 3 g. during an hour to a solution of

veratrylidene-1-hydrindone (2 g.) in acetic anhydride (35 c.c.). After 2 hours, the dark red mixture was added to a concentrated solution of ferric chloride in hydrochloric acid, and the precipitate was collected, dried, and extracted with acetic acid; the chocolate residue crystallised from absolute formic acid in brownish-red prisms, m. p. 237—238°, twinning characteristically with formation of a symmetrical cross (Found: C, 45·4; H, 3·2. $C_{18}H_{15}O_3Cl_4Fe$ requires C, 45·5; H, 3·1%). A similar, even more sparingly soluble, ferrichloride may be obtained analogously from piperonylidenehydrindone.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-6 : 7-*dimethoxybenzopyrylium Ferrichloride* (XII).—Anhydrous ferric chloride (10 g.) was gradually added to a mechanically stirred solution of 2-veratrylidene-5 : 6-dimethoxy-1-hydrindone (Perkin and Robinson, J., 1907, **91**, 1073) (3·7 g.) in acetic anhydride (50 c.c.) cooled in melting ice. After ½ hour, the vessel was removed from the cooling bath and a further equal quantity of sublimed ferric chloride added. After 15 minutes, the vessel was immersed in water at 40—50° and stirring continued for 20 minutes. Next day, decomposition with aqueous hydroferrichloric acid gave a gelatinous precipitate, which was collected and became crystalline on boiling with acetic acid. The substance crystallised from formic acid in deep brownish-crimson needles, m. p. 246—247°, with bluish-green reflex (Found: C, 45·0; H, 3·7. $C_{20}H_{19}O_5Cl_4Fe$ requires C, 44·9; H, 3·6%). Solutions of this salt in alcohol or formic acid exhibit a phenomenal, greenish-yellow fluorescence. The substance is insoluble in cold acetic acid and sparingly soluble in formic acid.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-6 : 7-*methylenedioxybenzopyrylium Ferrichloride* (formula similar to XII).—Anhydrous ferric chloride (20 g.) was gradually added to a stirred solution of 2-piperonylidene-5 : 6-dimethoxy-1-hydrindone (3·5 g.) in acetic anhydride (50 c.c.) during 2 hours. The product, isolated in the usual manner, was extracted by acetic acid and crystallised from formic acid in hæmatite-red, microscopic prisms, m. p. 270° (decomp.) (Found: C, 43·6; H, 3·0. $C_{19}H_{15}O_5Cl_4Fe$ requires C, 43·8; H, 2·9%). This very sparingly soluble substance exhibits a vivid greenish-yellow fluorescence in formic acid solution.

2-(2 : 3-*Dimethoxybenzylidene*)-1-*hydrindone*,

$$C_6H_4\begin{<}CO\\CH_2\end{>}C{:}CH{\cdot}C_6H_3(OMe)_2.$$

—This substance was obtained in almost theoretical yield by the methylation of 2-hydroxy-3-methoxybenzylidenehydrindone (Lawson and Robinson, J., 1924, **125**, 207) by means of methyl sulphate and potassium hydroxide in alcoholic solution. It crystallises from

alcohol in pale yellow prisms, m. p. 124° (Found : C, 77·2; H, 5·3. $C_{18}H_{16}O_3$ requires C, 77·2; H, 5·7%).

2 : 3-*Indeno*(1 : 2)-5 : 6-*dimethoxybenzopyrylium Ferrichloride* (formula after XII).—Anhydrous ferric chloride (18 g.) was gradually added to a stirred solution of 2 : 3-dimethoxybenzylidenehydrindone (3 g.) in acetic anhydride (40 c.c.) during 1·5 hours. The product, isolated in the usual manner, crystallised from acetic acid in crimson leaflets or flat needles, m. p. 168° (Found : C, 45·2; H, 3·3. $C_{18}H_{15}O_3Cl_4Fe$ requires C, 45·5; H, 3·1%). This salt does not exhibit strong fluorescence in any solution. *o*-Veratrylidenehydrindone might have given indeno-8-methoxybenzopyrylium ferrichloride, m. p. 187° (Lawson and Robinson, *loc. cit.*), by hydrolysis of the *o*-situated methoxyl group, but a mixture of the salts, m. p. 168° and 187°, melted indefinitely at about 140°.

2′ : 3′ : 5 : 6-*Tetramethoxy*-2-*benzylidene*-1-*hydrindone*,

$$C_6H_2(OMe)_2\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle C{:}CH{\cdot}C_6H_3(OMe)_2.$$

—The coppery-red potassium salt, resulting from the condensation of *o*-vanillin and 5 : 6-dimethoxyhydrindone in alcoholic solution in presence of potassium hydroxide, was methylated by means of methyl sulphate. The product crystallised in glistening yellow leaflets, m. p. 183—184°, from ethyl acetate–methyl alcohol (Found : C, 70·5; H, 5·2. $C_{20}H_{20}O_5$ requires C, 70·8; H, 5·6%). Anhydrous ferric chloride and acetic anhydride convert this substance into a ferrichloride crystallising from formic acid in brick-red leaflets, m. p. 211° (decomp.). The m. p. of the salt described below is depressed by admixture with this compound, and the salt, m. p. 211°, is therefore, in all probability, 2 : 3[5 : 6-*dimethoxyindeno*-(1 : 2)]-5 : 6-*dimethoxybenzopyrylium ferrichloride*.

2 : 3[5 : 6-*Dimethoxyindeno*(1 : 2)]-8-*methoxybenzopyrylium Ferrichloride* (formula after XII).—A solution of equivalent quantities of *o*-vanillin and 5 : 6-dimethoxyhydrindone in acetic acid was saturated with hydrogen chloride for 2 hours; it was then diluted with water and a ferrichloride precipitated. The latter crystallised from much acetic acid in brownish-red needles, m. p. 250° (decomp.) (Found : C, 45·1; H, 3·6. $C_{19}H_{17}O_4Cl_4Fe$ requires C, 45·0; H, 3·3%). Solutions of this salt do not exhibit fluorescence.

We wish to thank the Chemical Society for a grant which has defrayed a part of the expense of this investigation.

THE UNIVERSITIES OF OXFORD AND MANCHESTER.

[*Received, January 14th,* 1926.]

NOTES.

Acetyl-o-phenylenediamine and Acetyl-1 : 2 : 3-benztriazole. By FRANK BELL and JOSEPH KENYON.

THE cumbrous procedure for the preparation of acetyl-*o*-phenylenediamine described by Leuchs (*Ber.*, 1907, **40**, 1085) can with advantage be replaced by the following simplified method. Aluminium amalgam is added to a solution of *o*-nitroacetanilide in moist ether until the yellow colour of the solution is discharged. Owing to its limited solubility in ether, acetyl-*o*-phenylenediamine separates from the solution along with aluminium hydroxide, from which it is extracted by means of boiling benzene. It separates from benzene in small, lustrous plates, m. p. 132°.

On addition of the calculated amount of sodium nitrite to a solution of this compound in hydrochloric acid, there is produced an immediate precipitate of acetyl-1 : 2 : 3-benztriazole, which crystallises from alcohol in compact needles, m. p. 51° (Found : $CH_3{\cdot}CO$, 26·7. $C_8H_7ON_3$ requires $CH_3{\cdot}CO$, 26·7%). Acetyl-1 : 2 : 3-benztriazole is hydrolysed with extreme ease to give 1 : 2 : 3-benztriazole (m. p. 98°), which on acetylation reforms the acetyl derivative of m. p. 51°.—BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, February 23rd*, 1926.]

Density of Boric Oxide from a Fractional Crystallisation of Boric Acid. By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON, and GEORGE EDWARD STEPHENSON.

A PREVIOUS communication (Briscoe, Robinson, and Stephenson, J., 1925, **127**, 155) described a systematic fractional crystallisation of boric acid, involving about 1150 crystallisations. As the analytical method then applied proved useless to detect any differences in the atomic weight of boron resulting from this treatment, two end-fractions of boric acid which were still available were converted into boric oxide glass and the densities of these samples were compared by the flotation method recently described (*idem*, this vol., p. 70). The flotation liquid was the mixture of pentachloroethane and trimethylene bromide previously used having $d_4^{17\cdot00^\circ}$ 1·79773 and $d_4^{19\cdot45^\circ}$ 1·79372.

The data and results are as follows :

Origin of Sample.	Flotation Temp.	Density.	Relative Atomic weight.
Head Fraction Series B	18·18°	1·79415	10·790
Tail Fraction Series B	19·00	1·79445	10·796

In these determinations, the beads of each sample showed rather greater variations in density among themselves than did those derived from the various mineral sources (except sample No. 6) described in the previous communication. Therefore the authors attach little value to the third decimal figure in the present results and consider that these simply serve to indicate, in consonance with the results of a previous investigation on bromine (Robinson and Briscoe, J., 1925, **127**, 138), that fractional crystallisation of boric acid has produced no change as great as 0·01 in the atomic weight of boron.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (G. E. S.) to take part in this work.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, March 12th*, 1926.]

A Synthesis of 1 : 2-*Dihydroquinaldine. A Correction.* By FREDERICK ALFRED MASON.

IN a previous communication (J., 1925, **127**, 1032), a description was given of a synthesis of "1 : 2-dihydroquinaldine," having the properties of the substance recorded by Räth (*Ber.*, 1924, **57**, 555). As subsequent work (*e.g.*, Meisenheimer and Stolz, *Ber.*, 1925, **58**, 2330; König and Buchheim, *ibid.*, p. 2868) has cast doubts upon the validity of some of Räth's results, a re-examination of the present author's product has been made. The melting points of the recrystallised picrates of the "1 : 2-dihydroquinaldine" and of quinaldine were carefully compared and no depression was observed on admixture, so that the product obtained by the author and described as 1 : 2-dihydroquinaldine was in fact a mixture consisting largely of quinaldine itself, and the prefix "1 : 2-dihydro" should accordingly be deleted from the title. From the results of the previous analysis, which agreed almost exactly with the theoretical figures for dihydroquinaldine (0·0882 g. gave 0·2674 g. CO_2 and 0·0605 g. H_2O: C, 82·7; H, 7·6%. 0·1451 g. gave 12·4 c.c. N_2 at 18° and 754 mm. N, 9·7%) it now seems certain that the product obtained was a mixture of quinaldine and a hydrogenated substance, possibly tetrahydroquinaldine or *iso*butylaniline. This would agree with the work of Jones and Evans (J., 1911, **99**, 334), who showed that the so-called "aldol base" from *p*-toluidine gave, on treatment with acids, a mixture of 2 : 6-dimethylquinoline and 2 : 6-dimethyltetrahydroquinoline; similar results were obtained with the "aldol base" from *m*-xylidine (compare also Mills, Harris, and Lambourne, J., 1921, **119**, 1924).

Owing to the small amount dealt with, attempts to separate the

mixture were unsuccessful; its exact composition can be settled only by further investigation with larger quantities of material.—DYSON PERRINS LABORATORY, OXFORD. [*Received, March 8th,* 1926.]

The Reduction of Ethyl Dibenzylacetoacetate. By ELLEN SUSAN HILL.

DIALKYL- and diaryl-substitution products of ethyl acetoacetate should, theoretically, be convertible into quaternary hydrocarbons by well-known general reactions; ethyl dibenzylacetoacetate, for example, might be transformed into ethyl*iso*propyldibenzylmethane:

$$CH_3{\cdot}CO{\cdot}C(CH_2Ph)_2{\cdot}CO_2Et \longrightarrow CH_3{\cdot}CH(OH){\cdot}C(CH_2Ph)_2{\cdot}CO_2Et \longrightarrow CEt(CH_2Ph)_2{\cdot}CMe_2{\cdot}OH \longrightarrow CEt(CH_2Ph)_2{\cdot}CHMe_2.$$

Many attempts to carry out the first of these stages have been made; an alcoholic solution of the ester was treated with sodium, sodium amalgam, zinc and acids, hydrogen and colloidal platinum, amalgamated zinc and acids; and the ester was treated with sodium and amyl alcohol, but the only products isolated were the unchanged substance and an acid, m. p. 89° (see below). The ester was also unattacked by phosphorus pentachloride and therefore could not be reduced indirectly through the dichloro-derivative. Its stability under the conditions noted suggests steric hindrance.

By the action of sodium (twenty times the theoretical) on an ethereal solution of the ester floating on sodium hydroxide solution, two additional products were isolated. One of these was a neutral oil distilling at about 290° and probably dibenzylacetone (C, 84·6; H, 7·2; *M*, 212. $C_{17}H_{18}O$ requires C, 85·7; H, 7·4%; *M*, 238), and the other an acid, crystallising from light petroleum, melting at 152—153° and probably hydroxyethyldibenzylacetic acid (Found: Ag, 27·6. $C_{18}H_{19}O_3Ag$ requires Ag, 27·6%). The yields were so small that the compounds were not fully identified.

In attempting to prepare ethyl dibenzylacetoacetate (m. p. 57°) by the action of benzyl chloride on a methyl-alcoholic solution of sodium methoxide an ester melting at 41° was obtained. This was proved to be *methyl dibenzylacetate* by preparing it from dibenzylacetic acid (m. p. 89°) and methyl alcohol. The acid (m. p. 89°) obtained by the hydrolysis of ethyl dibenzylacetoacetate was proved to be dibenzylacetic acid; it would seem, therefore, that the compound described by Fittig and Christ as dibenzylacetoacetic acid (*Annalen*, 1892, **268**, 123) is really dibenzylacetic acid.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 21st,* 1926.]

Synthesis of Naphthathioxins. By REGINALD CHILD and SAMUEL SMILES.

LESSER and GAD have recently described (*Ber.*, 1925, **58**, 2557) experiments on the synthesis of αβ′-naphthathioxin; the present note gives the results of experiments made previously with a similar object. Di-β-naphthyl ether when heated with sulphur and a trace of iodine at 280° for 3 hours, or when treated with sulphur chloride and aluminium chloride, gave small quantities of αα′-naphthathioxin (m. p. 165°), which was isolated by means of the picrate. On the other hand, in accordance with the experience of Lesser and Gad, attempts to obtain αβ′-naphthathioxin by similar treatment of α-naphthyl β-naphthyl ether were unsuccessful. Lesser and Gad obtained 4-chloro-α-naphthyl β-naphthyl 2 : 1′-sulphide by treating a mixture of β-naphthol and 4-chloro-α-naphthol with sulphur chloride; but the substance is readily obtained in quantity from the reaction of β-naphthol with 4-chloro-α-naphthyl 2-sulphur bromide, the latter substance being formed from bromine and the corresponding disulphide in carbon tetrachloride. The corresponding sulphur chloride could not be obtained, owing to the ease with which chlorine displaces sulphur from the disulphide. Treatment of the foregoing αβ′-sulphide with dehydrating agents gave a small yield of a substance (m. p. 157°) which from its properties appears to be a naphthathioxin.—KING'S COLLEGE, LONDON. [*Received, February 3rd*, 1926.]

Critical Temperature of Mercury. By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

APPLYING the law of Guldberg and Guye (*Z. physikal. Chem.*, 1890, **5**, 374, etc.), that the critical temperature of a non-associated liquid is one and a half times its normal boiling point when both constants are expressed on the absolute scale, to the case of mercury, we should conclude that its critical temperature is 675°. From a brief note in a paper by Traube and Teichner (*Ann. Physik*, 1904, **13**, 620) it would appear, however, that this temperature is above 1000°. Further, calculation from surface tension data indicates that it is about 1550° (Journeau, *Bull. Soc. chim.*, 1924, **35**, 1293). This figure is so widely different from that given by the Guldberg and Guye law that it seemed advisable to make a further attempt to measure the critical temperature experimentally.

For this purpose, pure redistilled mercury was enclosed in a capillary tube of transparent silica having a bore of 2 mm. and walls 3 mm. in thickness. One end of the tube was sealed off, and

the other was attached to " Hyvac " and mercury diffusion pumps while the mercury was boiled and recondensed several times to free it from dissolved gases. Finally, a portion of the tube 4 cm. long was sealed off, containing a column of mercury 1 cm. long. This silica " bomb " was supported vertically in the middle of a horizontal iron pipe 30 cm. long and 5 cm. in internal diameter, which was heated electrically by a winding of " nichrome " wire. The ends of the pipe were shielded by plate-glass and the bomb was closely observed by means of a telescope. At a temperature above 1000°, the bomb burst. Immediately before this occurred, the mercury, although at a bright red heat, was still liquid, the contrast being quite distinct between the opaque liquid and the perfectly transparent vapour.

In view of the above, the experimental determination of the critical temperature of mercury would seem to be a matter of great difficulty. It is suggested, however, that mercury might be enclosed in a very stout-walled silica vessel of considerable size and heated inductively to its critical temperature by high-frequency oscillatory currents circulating in its vicinity. It might thus be possible to heat the mercury to the critical temperature while the silica vessel was so far cooled by radiation and conduction that its strength would be maintained.

We desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of us (L. A. S.) to take part in this work.—ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [*Received, February 4th*, 1926.]

Some Organo-silicon Compounds. By RONALD RUMSEY WIDDOWSON.

OF certain organo-silicon compounds described by Hart (*Rep. Brit. Assoc.*, 1887, 661), one, obtained by the action of sodium on a mixture of ethylene dibromide and silicon tetrachloride, is called dichlorosilicoethylene dibromide, $(CH_2Br{\cdot}CH_2)_2SiCl_2$; another, produced from trimethylene dibromide in a similar manner, is described as trimethylenesilicon dichloride, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>SiCl_2$, and its product of hydrolysis as trimethylenesilicon oxide. A dark brown solid, obtained from a mixture of silicon tetrachloride and *o*-dichlorobenzene, is named di-*o*-diphenylenesilicium,

$$C_6H_4>Si<C_6H_4.$$

Although the evidence offered in the paper is by no means convincing, the " compounds " there described are recorded in Beilstein's " Handbuch."

At Professor Kipping's suggestion and under his supervision, the author has repeated very carefully some of Hart's experiments under the same conditions. From ethylene dibromide and from *o*-dichlorobenzene no silicon compounds were formed in appreciable quantities; experiments with trimethylene dibromide were not made. These facts, a study of Hart's paper, and the general results of recent work seem to show that the organo-silicon compounds mentioned above may with advantage be deleted from the literature (compare Bygdén, *Ber.*, 1915, **48**, 1236).—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, January 29th*, 1926.]

Deposition of Metallic Zinc on the Positive Pole of a Simple Voltaic Cell. By SPENCER ROBERT HUMBY and MICHAEL WILLCOX PERRIN.

SOME observations first made in 1924 seemed to indicate that in simple voltaic cells which were left in action for some time metallic zinc was deposited on the copper plates. A large number of experiments have shown that this is the case.

Zinc and copper dipping into dilute sulphuric acid or zinc sulphate solution were connected together externally as in a simple voltaic cell; after some time the copper became covered with a layer of metallic zinc.

The following pairs of metals were treated in exactly the same way: zinc and platinum, zinc and silver, zinc and lead, zinc and iron, iron and silver, and it was found that zinc was deposited upon platinum, silver, lead, or iron, and iron upon silver. In each case, the more electropositive metal was thus deposited on the more electronegative one.

In Daniell cells, also, after short-circuiting for some days, a deposit was obtained on the copper consisting of both copper (from the copper sulphate solution) and zinc.

In the case of the simple $Zn|H_2SO_4|Cu$ cell, zinc was deposited while the liquid in the cell was still acid. In another experiment, the liquid was stirred by bubbling hydrogen through it, but this made no difference to the results. The zinc was deposited slowly and continuously, as was shown by weighing a platinum plate at intervals during the course of the experiment. When the two poles of the cell were disconnected, the zinc was dissolved off the copper provided the solution still remained acid.

The current with a $Zn|ZnSO_4|Cu$ cell fell to 0·006 amp. almost immediately and then more slowly to 0·0001 amp. in 30 minutes.

Various papers were found bearing on the subject. Odling (*Quart. J. Chem. Soc.*, 1857, **9**, 289) states that in several instances

if a metal is immersed in a strong, boiling and rather acid solution of a salt of a more electropositive metal, that metal is deposited out of solution on the first, or more electronegative, metal. Raoult (*Compt. rend.*, 1873, **76**, 156) states that if pieces of gold and cadmium connected together are immersed in a boiling solution of cadmium sulphate or chloride, metallic cadmium is deposited on the gold. The gold may be replaced by copper and the cadmium by zinc or tin with the same results. Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 540) states that sodium and potassium, potassium and barium, and sodium and barium are reciprocally replaceable in their amalgams.

The results so far obtained leave no doubt as to the reality of the phenomenon, but it is hoped that additional data will shortly be ready for publication.—WINCHESTER COLLEGE and NEW COLLEGE, OXFORD. [*Received, January 28th*, 1926.]

The System Ammonium Acetate–Acetic Acid–Water. By RUTH SUGDEN.

IN addition to the acid acetate $NH_4C_2H_3O_2,C_2H_4O_2$, a hydrated complex of the composition $2NH_4C_2H_3O_2,3C_2H_4O_2,H_2O$ has been

FIG. 1.

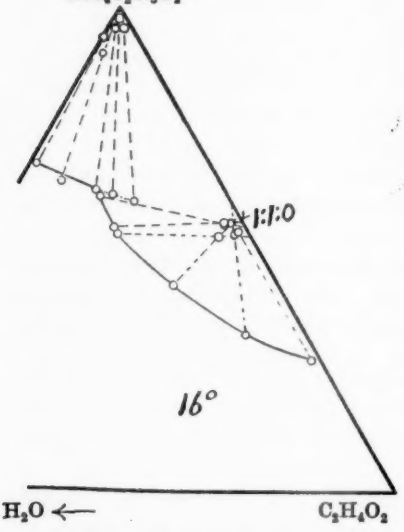
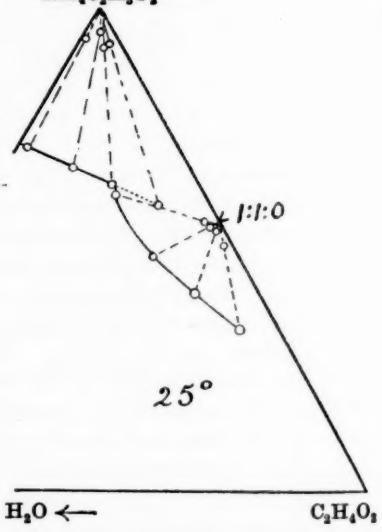


FIG. 2.



described by Berthelot (*Bull. Soc. chim.*, 1864, **22**, 440). At the suggestion of Professor Rivett, isotherms of the ternary system

have been determined at 16° and 25° and a few additional measurements made at 0°. Commercial chemicals (B.D.H., A.R.) were used. Analyses of saturated solutions and wet solids were carried out by the usual ammonia distillation method, a known excess of caustic soda being used from which, by back titration, the total acetate and hence the acetic acid present could be determined. Compositions in the following table are expressed in percentages of components by weight. Water (not quoted) may be obtained by difference.

% Composition of sat. soln.		% Composition of wet solid.		% Composition of sat. soln.		% Composition of wet solid.	
$NH_4C_2H_3O_2$.	$C_2H_4O_2$.	$NH_4C_2H_3O_2$.	$C_2H_4O_2$.	$NH_4C_2H_3O_2$.	$C_2H_4O_2$.	$NH_4C_2H_3O_2$.	$C_2H_4O_2$.
			Temperature 16.°				
67·8	0·91	94·4		55·6	21·7	55·3	41·3
64·4	7·73	90·9	1·46	54·3	22·7	53·0	41·6
62·6	16·0	96·6	0·96	42·5	38·1	54·6	42·8
*61·1	19·7	96·6	2·27	32·6	57·3	53·2	44·2
*59·6	23·9	96·5	2·20	27·3	72·3	53·7	44·3
61·1	17·1	55·0	41·5				
			Temperature 25°.				
70·6	2·15	94·2	1·17	60·7	23·2	55·5	42·6
67·0	12·0	95·7	2·77	48·5	36·2	54·6	43·4
63·3	21·1	92·3	5·1	41·0	47·6	54·3	45·0
*58·9	31·3	92·6	5·96	33·2	59·9	51·1	47·2
			Temperature 0°.				
63·8	3·7	94·5	2·38	48·9	19·6	53·6	45·7
*61·1	15·8	93·6	3·74	28·1	61·6	52·6	46·1

* Signifies metastable.

These figures are plotted in the diagrams, from which it is seen that the existence of the complex 1 : 1 : 0 is confirmed, but that there is no evidence whatever for the existence of Berthelot's compound 2 : 3 : 1 at the temperatures examined.—University of Melbourne. [*Received, February 8th,* 1926.]

ANNUAL GENERAL MEETING,

HELD IN THE CHEMISTRY THEATRE OF THE UNIVERSITY OF MANCHESTER ON THURSDAY, MARCH 25TH, 1926, AT 4 P.M.

DR. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, was in the Chair, and drew attention to the fact that this was the first occasion since the foundation of the Society in 1841 on which the Society had held its Annual General Meeting away from London.

The Report of the Council, together with the Balance Sheets and Statements of Accounts for 1925, was presented, and after a statement by the Treasurer, the adoption of the report and accounts was proposed by Prof. H. BRERETON BAKER, seconded by Dr. E. F. ARMSTRONG, and carried unanimously.

REPORT OF COUNCIL, 1925–1926.

I. *Fellowship Statistics.*

ON the 31st December, 1924, the number of Fellows was 3963. During the year 1925, 344 Fellows were elected and 10 reinstated, the gross total thus reaching 4317. The number of deaths recorded during the year was 40, as against 45 the previous year. The Council records a considerable falling off in the resignations received, the number being 88 as compared with 121 in 1924. The names of 105 Fellows have been removed from the List of Fellows owing to non-payment of annual subscriptions, and the election of one Fellow (in May 1924) has been declared void, the corresponding figures last year being 107 and 7, respectively. The number of Fellows at the 31st December, 1925, was, therefore, 4083, giving an increase of 120 over the preceding year. Among the Fellows who have died during the past year are Sir Edward Thorpe, who held the office of President from 1899–1901, of Treasurer from 1889–1899 and served on the Council for 40 years in all; Dr. Horace T. Brown, who was Treasurer from 1903–1904, Foreign Secretary from 1907–1913, and served on the Council for 20 years, and Professor F. R. Japp, who was Foreign Secretary from 1885–1891, and served on the Council for 16 years. The Council also mourns the loss of two distinguished Honorary Fellows, Professor Albin Haller (elected in 1908) and Professor Guglielmo Körner (elected 1898), the number of Honorary Fellows now being 24.

An obituary notice of Professor Körner, prepared by Professor J. B. Cohen, appeared in the Journal for December, and a notice of Professor Haller will be published in a forthcoming issue of the Journal. The Council takes this opportunity of recording its

appreciative thanks to those Fellows who kindly prepare for the Journal valuable notices of deceased Fellows.

The congratulations of the Council have been conveyed to Sir William A. Tilden (elected 1st June, 1865) and to Mr. William E. Bickerdike (elected 7th December, 1865), who have been Fellows for 60 years, and to the following, who, during the year, have attained their jubilee as Fellows :

	Elected.
Alfred Southall	May 6th, 1875.
Pattinson B. Melmore	May 20th, 1875.
Sir Dugald Clerk	May 20th, 1875.
G. William Davey	Nov. 18th, 1875.
John F. M. H. Stone	Dec. 2nd, 1875.
Sir Ernest H. Cook	Dec. 2nd, 1875.
Alfred Smetham	Dec. 16th, 1875.
Bernard Dyer	Dec. 16th, 1875.
William H. Watson	Jan. 20th, 1876.
Martin F. Roberts	Jan. 20th, 1876.
H. Wilson Hake	Jan. 20th, 1876.
William Foulkes Lowe	Feb. 3rd, 1876.
Harold Baily Dixon	Feb. 3rd, 1876.
William A. Smith	Feb. 3rd, 1876.
Paul G. W. Typke	Feb. 17th, 1876.
Francis S. Earp	Feb. 17th, 1876.
John M. H. Munro	Feb. 17th, 1876.

The congratulations of the Society were conveyed to Professor B. Brauner on the occasion of the celebration of his 70th birthday held in Prague in May.

II. *Changes in Officers.*

The Council has received with deep regret the resignation of Dr. Arthur W. Crossley from the office of President, owing to reasons of ill-health. The Council, in placing on record its warm appreciation of his eminent services and untiring devotion to the affairs of the Society, desires to express its best hope that his recovery may be speedy and complete.

III. *Publications.*

The Journal for 1925 contains 2986 pages, of which 2902 pages are occupied by 409 memoirs and 32 notes, the remaining 84 pages being devoted to Obituary Notices, one lecture, the Report on International Atomic Weights, the Report of the General Meeting, and the Presidential Address. The volume of the preceding year contained 363 memoirs and 31 notes, occupying 2605 pages. The number of papers published in the Journal for 1925 is a record, the previous largest number being 400 memoirs and 11 notes, occupying 3258 pages of the Journal for 1923.

During 1925, 479 papers were considered by the Publication Committee; of these, 37 were declined.

The average interval between the dates of receipt and of publication of papers was 13 weeks in 1925 and 17 weeks in 1924.

A large amount of work is done willingly and efficiently by Referees, and the Council desires to place on record its appreciation of their services. The Council also desires to express its thanks to Professor Wynne for again seeing the August number of the Journal through the press, thus enabling the Editor to take some holiday. It feels, however, that the arrangements for editing the Journal are far from satisfactory so long as the work remains in one pair of hands. Under present conditions the Editor, in the absence of voluntary assistance, would be debarred from a holiday, and, in the event of accident or illness happening to him, there is no one to take over the editorial work until his return to duty. This matter is receiving the attention of the Council.

IV. *Library.*

During 1925 there were 6994 attendances in the Library as compared with 6652 in 1924, 4746 of these being made by Fellows of the Society, and 2248 by members of contributing Societies, while the number of books borrowed was 4950 as against 4509 the previous year. The Library has been increased by the addition of 265 books, 609 volumes of periodicals, and 163 pamphlets, the corresponding figures last year being 265, 560, and 164, respectively. The Library now contains 30,011 volumes, consisting of 9066 books and 20,945 bound volumes of periodicals.

In 1925 £1799 2*s*. 3*d*. was expended on the Library, towards which £681 15*s*. was contributed by the kindred Societies. The Council desires again to express its appreciation of the substantial help received from the contributing Societies. The assistance thus given facilitates progress towards the establishment of a complete chemical library.

The urgent need for additional space for the Library has been mentioned in recent reports, and the necessity for a workroom for cataloguing and repairing books is hardly less urgent. For the moment the question of Chemistry House is in abeyance, so that relief in that direction is unlikely in the near future. It has been decided to provide further shelf space for books by lining the north and east walls of the Council Room with adjustable steel bookshelves and erecting a cantilever gallery. The consent of His Majesty's Office of Works having been obtained, the work will be put in hand without delay. It is estimated that the cost will be about £250, and that the shelf space thus provided may be

sufficient to meet the demands of the Library for three, or perhaps four, years. In this connexion it will be necessary to remove the portraits of the Past Presidents now in the Council Room. These will be contained in a portfolio accessible to Fellows, and the names of the Past-Presidents will be inscribed on oak panels which will be placed on the wall in the Meeting Room.

Arrangements have been made during the year by which readers can obtain photostatic copies of printed matter in the Library. Considerable use has been made of the facilities thus afforded.

V. *General.*

The society was represented by a number of Fellows at the meeting held at the Royal Institution on June 16th to celebrate the discovery of benzene by Faraday. On behalf of the President, who was unavoidably prevented from attending as official representative, Sir William Pope presented an Address of Congratulation. Professor C. S. Gibson, Mr. A. J. Greenaway, and Sir William Pope attended as delegates of the Society the Fifth Congress of Applied Chemistry held in Paris in September, and Professor H. E. Armstrong gave an oration in honour of Chevreul at the Celebrations held in the same city a month later; while Professor J. B. Cohen was the Society's representative at the Celebrations of the 11th centenary of the foundation of Pavia University held in Pavia in May. At the invitation of the General Council of Medical Education and Registration, the Council appointed the President and Foreign Secretary to represent the Society at the Conference held in February to discuss general questions relating to the proposed revision of the British Pharmacopœia. Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe were appointed to represent the Society on the Federal Council for 1926; while Professor J. W. McBain and Professor J. C. Philip were reappointed for a further term of two years on the Editorial Board of the "Journal of Physical Chemistry."

The Society has continued to be represented on the Bureau of Chemical Abstracts by Professors C. S. Gibson, G. T. Morgan, J. F. Thorpe, and W. P. Wynne. During the year the Bureau's proposals for the change of the format of the abstracts in pure chemistry were accepted by the Council, and accordingly from January, 1926, onwards, "British Chemical Abstracts" is appearing in two sections dealing respectively with papers in pure and applied chemistry, in double-column quarto format, and without overlap in respect of the papers abstracted. These arrangements make possible the preparation of a single annual index covering the abstracts in both sections, and this index will be supplied (without

additional charge) to all who receive the "A" section or the "B" section or both. Fellows of the Chemical Society, who are not members of the Society of Chemical Industry, but who desire to receive the "B" abstracts, can obtain them for £2 2*s*. per annum.

The Anniversary Dinner was held at the Hotel Victoria on March 26th, 1925, Dr. Arthur W. Crossley, President, in the chair. The company present numbered 240.

This year, for the first time in the history of the Society, it has been decided to hold the Annual General Meeting and the Dinner elsewhere than in London, and arrangements have been made for both to take place in Manchester—the meeting in the University and the Dinner at the Midland Hotel. It is hoped this innovation will commend itself to country members, and that the attendance will be such as to justify the Council in holding the Annual General Meeting at other provincial centres from time to time.

The Special Lecture this session was delivered on February 11th in the Chemistry Theatre of University College, London, by Professor J. Barcroft, who chose as his subject "Hæmoglobin." Instead of arranging for an additional Special Lecture, the Council decided to try the experiment of holding informal lectures given by Fellows of the Society, and two such lectures have been arranged. The first, by Professor R. Robinson, who lectured on "Recent Researches on the Structural Relationships of some Plant Products," was held in the rooms of the Society on November 26th at 6 o'clock, instead of the usual hour of 8 p.m.; the second lecture will be delivered by Professor W. E. S. Turner on April 29th at 6 p.m.

The large attendance at the lectures indicates that they are appreciated, and the Council desires to express its warm thanks to those who place their services at the disposal of the Society in this connexion.

The hope expressed in the last Report that the difficulty in awarding the Harrison Memorial Prize might be overcome by an agreement with the Committee which promoted the memorial, to vary the terms of the Trust Deed by the omission of the latter part of Clause 9, has not yet been realised.

The Council has made a grant of £100, thus completing the £300 promised, towards the cost of publishing the "Annual Tables of Constants," and has contributed £50 towards the cost of the Scientific Exhibit at the British Empire Exhibition, 1925. By means of the Russian Fund, which was created in September 1921 to grant relief to Russian Men of Science and their dependents, the Council has been able to afford assistance to Madame Mendeléev. A letter of thanks from Madame Mendeléev appeared in the

Proceedings for 1926 (p. 2). The Russian Fund, which reached a total of £400 4*s.* 10*d.*, has been closed, the balance of £7 7*s.* 10*d.* having been transferred to Publications Fund Account.

RUSSIAN FUND.

Statement of Income and Expenditure, 1921—1925.

Income.	£	*s.*	*d.*	*Expenditure.*	£	*s.*	*d.*	£	*s.*	*d.*
To Donations from Fellows	400	4	10	By Donations :						
				Prof. Mikkola . .	20	0	0			
				„ Tschugaeff .	1	0	0			
				„ Makovetzky .	171	4	0			
				„ Konovalov .	58	0	0			
				American Relief Fund . . .	28	13	11			
				Imperial War Relief Fund . . .	45	16	0			
				Madame Mendeléev	45	15	0			
								370	8	11
				Printing				9	11	6
				Scientific Books				1	6	3
				Carriage of Books and Clothing .				9	18	1
				Bankers' charges				1	12	3
				Balance in hand				7	7	10
	£400	4	10					£400	4	10

JOCELYN THORPE,
Treasurer.

The List of Fellows, which, owing to the call for economy, was not published in 1924, was printed in August, 1925, and issued to those Fellows who made application.

In accordance with the decision of the Council, copies of the Presidential Address, entitled " Universities as Centres of Chemical Research," delivered by Professor W. P. Wynne on March 26th, were distributed amongst Members of Parliament, various Government Officials, and educational bodies.

The attention of the Council has been directed to the use by Fellows of the letters " F.C.S." in advertisements. The Council deprecates the use of the letters in this connexion, since they do not denote a qualification and such use is misleading to the public.

Applications for Research Grants aggregating £1644 have been received during the year, and Grants amounting to £758 10*s.*, as recorded in the Proceedings (see pp. 93 and 148), have been allotted. Since the total sum for which application was made far exceeded that available for distribution, prior consideration has been given to applications made by Fellows.

VI. *Financial.*

The balance representing excess of income over expenditure for 1925 is £466 4*s*. 3*d*. The income of the Society has increased by £1208 6*s*. 8*d*. over that of 1924, in spite of the fact that the admission fees (£528 in 1924) have not been available, and that there has been a diminution in income from advertisements (£25 3*s*. 7*d*.), from invested funds (£37 4*s*. 11*d*.), and from miscellaneous receipts and sales (£138). The source of the new income is to be traced to the decisions of the Council, reached in 1923 and in 1924, to charge an increased price for the Journal, Abstracts, and Annual Reports to the public, and to charge Fellows for the Annual Reports; also, for the first time there has been a substantial income from the Publications Fund. The total obtained under these heads during the year has been £6112 8*s*. 8*d*., as against £4522 17*s*. 10*d*. for 1924 (during which year some of the effects of the changes were beginning to be felt), and £3799 17*s*. 6*d*. for the previous year, that is, before the changes came into operation.

The expenditure side of the account shows that the cost of the Journal has increased by £223 12*s*. 3*d*., despite the fact that there has been a saving of £125 16*s*. on the preparation of Authors' copies. The cause of this increase is the enlargement of the Journal by 288 pages due to the publication of 409 memoirs in place of the 363 published in 1924. The cost of the Abstracts has increased by £394 17*s*. 8*d*., due to the number of pages in 1925 being 468 higher than in 1924. There is, however, no overlapping in the payment of editorial salaries, and for this reason a saving of £113 9*s*. 9*d*. has been effected. Judging by these figures it is evident that there is still an upward tendency in the curve representing the world's annual output of published chemical research, and that the apex of the curve has still to be attained. At the same time there seems to be no immediate prospect of the cost of printing being materially decreased and, until the curve flattens, the Society will have to meet a constantly rising expenditure.

Among the other items on the expenditure side it will be noticed that the administration expenses have increased by £190 2*s*. 7*d*., due, mainly, to an increase in the item for miscellaneous printing and stationery of £125 0*s*. 6*d*. It will be seen, however, that the cost of printing the List of Fellows has been more than met by a saving of £133 1*s*. 4*d*. in the cost of the Annual Reports.

The total market value of the invested funds of the Society is £40,474 10*s*. 5*d*., an increase of £1,709 3*s*. 4*d*. over the figure for 1924 despite the depreciation of trustee stock to the extent of £852 on the General Purposes Account and the sale of £662 7*s*. of 3½% Conversion Stock, value £500, from the Research Fund Account.

The outlook for the future is fairly promising because, during the year 1926, the full interest on the Pedler bequest will become available; moreover it is to be expected that increased receipts will be obtained from outside sales of publications. On the other hand, the Society will be faced with an increased expenditure due to the scheme for the superannuation of the staff, and also to the cost of fitting the Council Chamber with bookcases in order to meet the requirements of the library. Next year's balance will depend on the cost of the Journal and Abstracts, and it is to be hoped that the scheme of co-operation which has led to the founding of the Bureau of Chemical Abstracts will enable a saving to be made by the elimination of the overlap between the "A" and the "B" series.

Publications Fund. In the last report of Council it was stated that, notwithstanding the generous response by Fellows who had contributed £1434 17*s.* 1*d.* to the Publications Fund, if the Fund were to be made really effective it would be necessary substantially to increase it. With this object in view it was decided to issue an appeal to Manufacturers, and as a result the Publications Fund now stands at £4067 17*s.* 4*d.* Of this, £2166 was received from Manufacturers and other firms connected directly and indirectly with the Chemical Industries of the country and £100 as a grant from the Birmingham University Research Fund. The income derived from the Publications Fund, together with Subscriptions received during the year under review, amounts to £622 13*s.* 10*d.* This sum, in which are included £350 from the Government Publications Grant of the Royal Society, and £80 the income from the residue of the estate of the late Sir Alexander Pedler, has helped to meet the expenses of publication. It is anticipated that between £4000 and £5000 bequeathed to the Society by Sir Alexander Pedler will be made over to the Society during 1926; the Publications Fund will then have a capital sum of close upon £9000.

Special Publications Fund. In 1918, a Committee of Chemists was formed to prepare and publish chemical bibliographies and works of reference in the English language, and funds were collected. The scheme was abandoned, but funds amounting to £1896 8*s.* 4*d.* collected by this Committee have been handed over to the Society on the understanding that they would be used "for the purpose of promoting chemical publication, but not for the purpose of defraying the cost of the Society's ordinary publications." The Council accepted the funds on the conditions stated, and a Special Publications Fund has been created, the sum of £1600 being invested in Conversion Loan.

Memorial Lectures. During the year Vol. I of the Memorial Lectures has been reproduced by a phototype process and is sold

to Fellows at 9*s*., post free, and to the Public at 10*s*. 6*d*. The publication of this volume is being financed by means of the Special Publications Fund.

Staff Superannuation Scheme. Another matter which has received the serious consideration of the Council has been the necessity for making some provision towards the Superannuation of the Staff. A contributory scheme of insurance based upon a 10 per cent. premium of the salaries received by the Staff, and payable at death, or on retirement, has been instituted, 5 per cent. being contributed by members of the staff and 5 per cent. by the Society. It is realised, however, that the sums thus accruing on the retirement of the beneficiaries will be inadequate, and accordingly a Pensions Fund has been created with a view to amplifying the amounts received from the insurance policies. The general funds of the Society will thus be relieved from any sudden call they may have to face, and Fellows have been invited to contribute to the Fund.

Sales of Publications. The price to the Public of the "A" Abstracts in Pure Chemistry for 1926 has been increased from £2 10*s*. to £3 10*s*., and the price of the Journal and Abstracts together has been increased from £5 to £5 10*s*. to the Public, and from £4 5*s*. to £4 15*s*. to Fellows who require extra copies. In order that the Abstracts in the new format may reach the Fellows in as good condition as possible it has been decided to issue them flat and in envelopes.

Advertisements. It is hoped that with the increased facilities which the "A" Abstracts in the new format afford for displaying announcements, the income of the Society derived from advertisements will show a considerable increase in the forthcoming year.

A vote of thanks to the Auditors (Profs. J. F. Spencer, A. J. Allmand, and J. S. S. Brame) for their services, was proposed by the Treasurer, seconded by Prof. F. L. Pyman, and carried unanimously.

Prof. H. B. Dixon proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the year. This was seconded by Dr. Alfred Rée and adopted, acknowledgment being made by Sir William Pope.

On the motion of Prof. R. Robinson, seconded by Dr. D. C. Henry, Prof. A. J. Allmand, Prof. J. S. S. Brame, and Dr. G. W. Monier-Williams were elected Auditors for the coming year.

Prof. T. S. Patterson then moved the following resolution:

"In view of the fact that the publication in the Proceedings of the Chemical Society of a list of titles of papers which have been received but not published and which—either because the Publication Committee considers them unsuitable or because the author

may be unable to accept alterations suggested by the referees or by the Publication Committee, or for any other reason—may not be published, is very prejudicial to the subsequent publication of these papers elsewhere and, by disclosing the fact that such work is in progress, unfair to the author, besides involving the Society in unnecessary and unjustifiable expense at a time when all possible economy should be exercised, this meeting recommends that the practice of publishing such a list be discontinued."

This was seconded by Prof. F. J. WILSON and, after discussion, was put to the meeting, and declared lost.

The following resolution :

"That this meeting, being of opinion that the position of the Chemical Society would be strengthened and the membership increased by the institution of local sections, recommends the Council to take such steps as would render practicable the institution of local sections where they might be desired"

also proposed by Prof. T. S. PATTERSON and seconded by Prof. F. J. WILSON, was discussed; on its being put to the meeting it was declared lost.

THE PRESIDENT then delivered his address, entitled "The Co-operation of Science and Industry."

A vote of thanks to the President for his services in the chair during the past year, and for his address, requesting him to allow the address to appear in the Journal, was proposed by Prof. W. P. WYNNE, seconded by Prof. W. H. PERKIN, and carried with acclamation. The PRESIDENT acknowledged the thanks and proceeded to read the report on the election to vacancies on the Council, announcing that Prof. H. Brereton Baker had been elected President. Prof. Baker then took the chair and continued the reading of the report :

Vice-Presidents who have filled the office of President.—H. E. Armstrong; Arthur W. Crossley; Percy F. Frankland; W. H. Perkin; Alexander Scott; W. P. Wynne.

Vice-Presidents who have not filled the office of President.—J. B. Cohen; A. J. Greenaway; James C. Philip; Sir Robert Robertson; R. Robinson; N. V. Sidgwick.

Treasurer.—Jocelyn F. Thorpe.

Secretaries.—T. Slater Price; C. S. Gibson.

Foreign Secretary.—F. G. Donnan.

Ordinary Members of Council.—H. Bassett; D. R. Boyd; O. L. Brady; H. V. A. Briscoe; A. E. Dunstan; F. A. Freeth; F. W. Gamble; R. Whytlaw Gray; J. Kenyon; B. Lambert; T. S. Moore; T. J. Nolan; K. J. P. Orton; R. H. Pickard; B. D. Porritt; F. L. Pyman; G. Stubbs; F. J. Wilson.

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d.
To Life Compositions		123 0 0
„ Annual Subscriptions :—		
Received in advance, on account of 1925	1083 0 0	
„ during 1925 „ „	8130 0 0	
„ „ „ „ 1924	446 8 0	
„ „ „ „ 1923 and previous years	16 10 0	
	9675 18 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	500 0 0	
	9175 18 0	
Add Arrears at date : £901 10*s.* ; Estimated to realise as per Balance Sheet	500 0 0	
		9675 18 0
„ Investments, Dividends on :—		
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	24 11 11	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock, 1914/54	35 18 8	
£1400 India 2½ per cent. Stock	35 0 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	48 0 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	84 15 7	
£1200 Leeds Corporation 3 per cent. Stock	28 7 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	45 0 0	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	28 2 6	
£700 Canada 5½ per cent. Stock, 1930/50	19 5 10	
£2100 5 per cent. War Stock, 1929/47	105 0 0	
£1100 5 per cent. War Bonds, 1929/47	44 0 0	
£600 Funding Loan, 4 per cent., 1960/90	24 0 0	
£11873 3½ per cent. Conversion Stock	374 0 0	
„ Income Tax Recovered	137 5 3	
„ Interest on Deposit	51 4 11	
		1084 11 8
„ Publication Sales :—		
Journals and Proceedings	2663 11 0	
Abstracts	2067 0 7	
Collective Index, Vols. I–V	64 4 6	
Annual Reports on Progress of Chemistry	759 3 3	
Berichte	22 0 0	
	5575 19 4	
Less Publishers' Commission	513 19 9	
		5061 19 7
„ Proceeds of Advertisements in Journal and Abstracts	596 17 0	
Less Commission	57 11 8	
		539 5 4
„ Miscellaneous Receipts		25 10 9
„ Donations to Library :—		
Association of British Chemical Manufacturers	250 0 0	
Biochemical Society	10 10 0	
Faraday Society	5 5 0	
Institute of Brewing	45 0 0	
Institute of Chemistry	250 0 0	
Society of Chemical Industry	100 0 0	
Society of Dyers and Colourists	10 10 0	
Society of Public Analysts	10 10 0	
		681 15 0
„ Pedler Bequest, Income from Residue of Estate of Sir Alexander Pedler		80 0 0
„ Subscriptions from other Societies		28 17 6
„ Transfer from Publication Fund, viz. :—		
Government Publications Grant (through the Royal Society)	350 0 0	
Dividends and Interest on Deposit	184 3 4	
Subscriptions	88 10 6	
		622 13 10
		£17,923 11 8

FOR THE YEAR ENDED 31ST DECEMBER, 1925.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Editorial Salaries	869 0 0	
Editorial Postages	69 10 7	
Printing of Journal	3423 15 1	
Banding	69 7 5	
Printing of Advertisements	128 17 8	
Addressograph Labels	5 14 1	
Distribution of Journal	474 9 5	
Authors' Copies	312 8 9	
Insurance of Stock	5 5 0	
Warehousing of Stock	5 10 2	
		5363 18 2
,, Expenses on account of Abstracts :—		
Editorial Salaries	1085 0 0	
Editorial Postages	34 10 0	
Abstractors' Fees	1287 11 11	
Printing of Abstracts	3026 8 10	
Banding	69 7 4	
Addressograph Labels	5 14 2	
Distribution of Abstracts	474 9 5	
Insurance of Stock	5 5 0	
Warehousing of Stock	5 10 2	
Miscellaneous	61 17 2	
		6055 14 0
,, Lecture Expenses		27 11 6
,, Advance Proofs and Reports of Meetings		84 17 3
,, Annual Reports on the Progress of Chemistry		528 15 1
,, Purchase of Back Numbers of Journal		18 18 10
,, List of Fellows—Printing, etc.		126 2 0
,, Library Expenses :—		
Salaries	1185 10 0	
Books and Periodicals	483 7 6	
Binding	130 4 9	
		1799 2 3
,, Donations :—		
Annual Tables of Constants	100 0 0	
British Empire Exhibition	50 0 0	
		150 0 0
,, Administration Expenses :—		
Salaries of Staff	1427 12 9	
Wages (Commissionaire, Housekeeper, and Charwomen)	414 6 0	
Pensions	16 5 0	
Coal and Lighting	83 12 1	
House Expenses and Repairs	109 16 3	
Telephone	22 0 2	
Tea Expenses	43 0 3	
Insurances	25 0 4	
Accountants' Charges	31 10 0	
Commission on Recovery of Income Tax	6 17 3	
Miscellaneous Printing and Stationery	472 3 7	
Postages	201 13 1	
Legal Charges	10 10 0	
Carriage on Journals to Germany	16 7 11	
New Press and Renovating Seal	16 0 0	
Addresses	14 14 0	
Miscellaneous Expenses	80 8 3	
		2091 16 11
,, Transfer to Publications Fund (Life Composition Fees)		123 0 0
,, Publications Fund—Income from Pedler Bequest		80 0 0
,, Collective Index Vol. VI		112 11 5
,, Excess of Income over Expenditure carried to Balance Sheet		466 4 3
		£17,923 11 8

Research and other Funds Income and Expenditure Accounts for the Year ended 31st December, 1925.

RESEARCH FUND.

Income.

	£ s. d.	£ s. d.
To Dividends on:		
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	31 5 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	20 3 11	
£1142 16s. New South Wales 3 per cent. Debenture Stock	34 5 8	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2	
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	26 13 1	
£806 Victoria 3 per cent. Stock, 1929/49	19 0 10	
£4498 11s. 0d. 5 per cent. War Loan, 1929/47	224 18 6	
£5164 13s. 9d. 3½ per cent. Conversion Stock	192 7 0	
		582 7 2
,, Income Tax Recovered		50 17 4
,, Repayment of Grants		111 5 8
,, Interest on Deposit		4 17 0
,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		17 11 8
		£766 18 10

Expenditure.

	£ s. d.
By Grants	758 10 0
,, Commission on Recovery of Income Tax	2 10 10
,, Advertisements	5 18 0
	£766 18 10

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

To Dividends on:—		
£500 National War Bonds, 5 per cent., 1928	25 0 0	
£500 National War Bonds, 5 per cent., 1929	25 0 0	
£61 15s. 8d. Conversion Stock, 3½ per cent.	2 3 2	
Interest on Deposit	4 9 7	
	£56 12 9	
By Advertisements		2 4 6
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		54 8 3
		£56 12 9

PUBLICATIONS FUND.

Income.	£	s.	d.	*Expenditure.*	£	s.	d.	£	s.	d.
To Transfer from General Account, being Life Composition Fees for year	123	0	0	By Transfer to General Account—Income applicable to 1925 Publications, viz.:—						
,, Subscriptions	101	0	6	Government Publications Grant (through the Royal Society)	350	0	0			
,, Donations	2395	14	4	Dividends and Interest on Deposit	184	3	4			
,, Interest on Deposit	20	19	2	Subscriptions	88	10	6			
,, Government Publications Grant (through the Royal Society)	350	0	0					622	13	10
,, Dividend on £4623 4s. 9d Conversion Stock, 3½ per cent.	83	4	2	,, Subscriptions in advance				12	10	0
,, Transfer from General Purposes. Income from Pedler Bequest	80	0	0	,, Balance, being excess of Income over Expenditure, carried to Balance Sheet				2518	14	4
	£3153	18	2					£3153	18	2

SPECIAL PUBLICATIONS FUND.

	£	s.	d.		£	s.	d.
To Sales of Publications :—				By Cost of Reproduction :—			
Memorial Lectures, Vol. I	52	10	0	Memorial Lectures, Vol. I	225	3	0
,, Balance, being Excess of Expenditure over Income carried to Balance Sheet	172	13	0				
	£225	3	0		£225	3	0

STAFF PENSIONS FUND.

	£	s.	d.		£	s.	d.
To Subscriptions	15	15	0	By Excess of Income over Expenditure carried to Balance Sheet	15	15	0

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st DECEMBER, 1925.

GENERAL PURPOSES.

Liabilities	£ s. d.	£ s. d.
To Subscriptions received in advance		1060 10 0
,, Sundry Creditors (Printing and other Expenses)		2905 2 6
,, Excess of Assets over Liabilities as per last Balance Sheet	25,660 6 5	
Add Excess of Income over Expenditure for Year	466 4 3	
		26,126 10 8
		£30,092 3 2

Assets.	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£737 London, Midland and Scottish Railway 4 per cent. Debenture Stock	839 3 7	
£1520 14*s.* 3*d.* Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock, Bristol Dock Account	2070 2 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923-53	1460 13 6	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0	
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock, 1929/47	1995 0 0	
£1100 5 per cent. National War Bonds, 1929/47 ...	1045 0 2	
£600 4 per cent. Funding Loan, 1960/90	480 0 0	
£11,873 3½ per cent. Conversion Stock	8987 2 2	
(Market Value £21,732 3*s.* 2*d.*)		26,296 3 3
,, Sundry Debtors		2593 18 10
,, Subscriptions in Arrear £901 10*s.* Estimated to realise		500 0 0
,, Insurance paid in advance...		52 9 3
,, Cash in Hand		1 13 6
,, Cash at Bank		647 18 4
		£30,092 3 2

RESEARCH FUND.

	£ s. d.	£ s. d.
To Excess of Assets over Liabilities as per last Balance Sheet	14,462 4 2	
Less Excess of Expenditure over Income for Year	17 11 8	
		14,444 12 6
		£14,444 12 6

	£ s. d.	£ s. d.
By Investments (value when acquired):		
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
£1034 Great Western Railway 2½ per cent. Debentures	1049 15 11	
£1142 16*s.* 0*d.* New South Wales 3 per cent. Stock 1935	1000 0 0	
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	1009 18 9	
£806 Victoria 3 per cent. Stock, 1929/49	706 6 2	
£4498 11*s.* 0*d.* 5 per cent. War Stock, 1929/47	4267 4 10	
£5164 13*s.* 9*d.* 3½ per cent. Conversion Stock	3898 14 10	
(Market Value £12,574 12*s.* 10*d.*)		13,944 17 3
,, Cash at Bank ... ... Current Account	99 15 3	
Do. ... ... Deposit Account	400 0 0	
		499 15 3
		£14,444 12 6

THE EDWARD FRANK HARRISON MEMORIAL TRUST

	£ s. d.	£ s. d.
To Balance of Income		1 0 0
,, Excess of Assets over Liabilities as per last Balance Sheet	1,000 0 0	
Add Excess of Income over Expenditure for Year	1 0 0	
		1,001 0 0
		£1,002 0 0

	£ s. d.	£ s. d.
By Investments (value when acquired):		
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
(Market Value £1,000 0*s.* 0*d.*)		1010 0 0
,, Cash at Bank ... ... Current Account	1 0 0	
Do. ... ... Deposit Account	1 0 0	
		2 0 0
		£1,002 0 0

		£14,444 12 6			499 15 3
					£14,444 12 6

THE EDWARD FRANK HARRISON MEMORIAL TRUST

To Excess of Assets over Liabilities as per last Balance Sheet			1251	6	8		
Add Excess of Income over Expenditure for Year			54	8	3		
			£1305	14	11		
By Investments (value when acquired):—							
£500 National War Bonds 5 per cent. 1928			500	0	0		
£500 National War Bonds 5 per cent. 1929			500	0	0		
£61 15*s.* 8*d.* 3½ per cent. Conversion Stock (Market Value £1096 9*s.* 9*d.*)			50	1	5		
						1050	1 5
Cash at Bank — Current Account			55	13	6		
Do. — Deposit Account			200	0	0		
						255	13 6
						£1305	14 11

PUBLICATIONS FUND

To Subscriptions received in advance				12	10	0	
,, Excess of Assets over Liabilities as per last Balance Sheet	1536	13	0				
Add Excess of Income over Expenditure for Year	2518	14	4				
				4055	7	4	
				£4067	17	4	
By Investment £4623 4*s.* 9*d.* 3½ per cent. Conversion Stock (Market Value £3478 19*s.* 9*d.*)						3500	0 0
,, Life Composition Fee						18	0 0
,, Cash at Bank on Current Account						549	17 4
						£4067	17 4

SPECIAL PUBLICATIONS FUND

To Funds in the hands of the Chemical Publication Committee—Transferred	1896	8	4				
Less Excess of Expenditure over Income to 31st December, 1925	172	13	0				
				1723	15	4	
				£1723	15	4	
By Investments:—							
£2115 8*s.* 10*d.* 3½ per cent. Conversion Stock (Market Value £1592 4*s.* 11*d.*)						1600	0 0
,, Sundry Debtors for Sales:—							
Memorial Lectures Vol. I						45	15 0
,, Cash at Bank						78	0 4
						£1723	15 4

STAFF PENSIONS FUND

To Excess of Income over Expenditure						£15	15 0
By Cash at Bank						£15	15 0

K K

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant.

23, QUEEN VICTORIA STREET, E.C. 4
February 10th, 1926.

Approved { J. F. SPENCER. A. J. ALLMAND. J. S. S. BRAME.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING held in Manchester on March 25th, 1926.

By ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S.

THIS is the first occasion on which the Chemical Society has departed from a custom, which has persisted since its foundation in 1841, namely, that of holding all its official meetings at its premises in London. The opinion has often been expressed that our provincial members do not have a sufficient say in the management of the Society's affairs, and certain alterations of Bye-Laws have recently been made, which materially affect this state of affairs. When the suggestion was made to the Council that every alternate Annual Meeting should be held in the Provinces, it was unanimously accepted and it is by virtue of that decision of the Council that we meet to-day in Manchester.

It seems particularly appropriate that our meeting should be in this Institution and in this lecture theatre; for through the Professors who have taught here and who have also been Presidents of the Chemical Society there are very close ties with us, and I am confident that I may record the most grateful thanks of the Society to the University of Manchester for granting permission for us to assemble here to-day.

The first professor of chemistry in the Owens College was Edward Frankland (1851—1857), who was President of our Society from 1871—1873. For the twenty-nine succeeding years, 1857—1886, he was followed by Henry Enfield Roscoe, who was President of the Chemical Society in 1880—1882. It was my privilege to be one of the later students of Sir Henry Roscoe, and I have often heard him lecture in this room. He was truly a remarkable teacher and one who had a very unusual hold and influence on his students. He was not a polished lecturer from the point of view of delivery, nor because he gave deep-seated discourses into abstruse chemical problems, but he was a lecturer who had the faculty of interesting his students in a marked degree, in consequence of which they became anxious to learn for themselves. That, to my mind, is the essence of real teaching.

Roscoe was followed in 1886 by Harold Baily Dixon, who occupied the Chair for thirty-seven years, namely, until 1923, and who was President of our Society during the period 1909—1911. My main student years were spent under his direction, but since he is here with us to-day, I will only say of him that he is as young as ever,

still hale, hearty, and active. Long may he remain so! There is, however, one very special reason why we may to-day offer him our warmest congratulations, inasmuch as he was elected a Fellow of our Society in 1876 and has therefore attained his Jubilee of Fellowship.

Two other past Presidents of our Society have also been Professors in this University: Professor W. H. Perkin, who was Professor of Organic Chemistry from 1892—1912 and our President for the period 1913—1915, and Sir William Pope, who was Professor of Applied Chemistry from 1905—1908 and our President from 1917—1919. To them also we would express our sincere wishes for long-continued health and activity.

The Co-operation of Science and Industry.

It is a simple economic fact that since this country does not produce a sufficiency of foodstuffs to feed its population, it must manufacture goods and sell these in foreign markets at a profit, in order to purchase the food which is necessary to sustain life. The more the population grows, the more of our manufactured goods must be sold abroad, if our existence is to continue. It follows from this fact that the maintenance of our industries is a national necessity, and they must not only be maintained on the same standard as in the past, but we must always be attempting to reach a higher efficiency, in order to cope with foreign competition. There was a time when Great Britain, as the pioneer of industrial development, could afford to select her own pace and her own methods, for she alone was in the field. The results obtained, largely without the aid of science, were indeed astonishing, but they came as a result of the breaking of new ground. Virgin soil may give wonderful crops for a few years, but to take from it continually and give nothing to it spells, as everyone realises, ruination, and in order to maintain the harvest it is necessary to nurture the soil or to manure it.

British industry worked on virgin soil in the past, and has worked it well-nigh to starvation point, owing to the lack of appreciation of the importance of science generally from the point of view of our national welfare. Numberless examples of the importance of science to industry and to the general welfare of mankind have been and are being constantly brought to our notice, and the years 1914—1918 gave signs that the nation had at last realised that science and scientific method were our only hope. Yet the lesson then apparently learnt seems to have been forgotten, because as a nation we still fail to realise that all real industrial progress is the result of the application of scientific facts and data and that those

who fail to utilise science to the full must inevitably fall behind in the race of nations which is now in progress.

Instead of being, as in the past, almost the only industrial nation, we now realise that other peoples have become industrialists, to whom we have given all our past experience. But they have forged ahead owing to their full appreciation of the possibilities of science in its application to industrial problems; from being the teachers in the past, we have now become pupils, and not very apt or willing pupils at that. We do not seem able to forget our unprecedented and unopposed success in the past; we think the same methods should still lead to success now and in the future, and we waste much precious time in wondering why our industries are not as prosperous as they used to be.

We can scarcely look for more new raw material within the country other than brains, in which respect we have good reason to think that our raw materials are at least equal in quality to those of any other country. Our brains must be used to resuscitate our industrial soil, which must be nurtured or manured, and new scientific facts and data are the nourishment which must be given if industry is to continue to be a profitable undertaking; if we are to be, I will not say as successful as we were in the past, but if we are to hold a place amongst the foremost nations of the world, or if our existence as a nation is to continue.

An anonymous author writes * as follows in the *Round Table* under the heading "British Industry and the Future":

"It is not only in the actual processes of manufacture that 'science can be used, but in the whole conduct of business, from 'the purchase of raw materials and the distribution of machinery, 'to the training and selection of labour, transport and sales. All 'these problems are more or less solved by a business that pays 'its way, but in too many cases rule of thumb and antiquated 'methods make the yield much poorer than it might be. For 'the higher branches of management there is little or no systematic 'training attempted. . . . In an age of super competition nothing 'but the best-equipped brains will be able to stand the pace. . . . 'Modern industry is as complex and difficult a profession as any. 'Its leaders need as thorough and prolonged an intellectual train-'ing as the doctor or the lawyer."

If a country can manufacture goods of superior quality, of constant novelty or of exceptionally high performance, at reason-

* Several quotations in this paper are from an article entitled "British Industry and the Future," to be found in the September 1925 number of the *Round Table Review*: also from a pamphlet "What Price Progress", published by the "Chemical Foundation," New York, 1925.

able prices and keep on doing so, other countries are compelled to buy from it. Science is the modern key to such a situation and new discoveries in science are essential to maintain the industrial position of this country; in fact, science is the sentinel that must be posted at the door of every business house with the main object of preventing loss from want of knowledge. If we look round, surely nothing can bring greater hope to us than the realisation of the many comforts we enjoy as the result of research—electric light, the telephone, the telegraph, wireless, the internal combustion engine, to mention only a few of the more obvious.

But on one point let there be no doubt; although science should bring great hope to all for the future, it gives no hope whatever for less strenuous efforts, but rather the reverse. Science of all taskmasters is the hardest, the most uncompromising, the most severe, punishing relentlessly any slack or slovenly work done in her name and exacting to the uttermost limit faithful and untiring devotion, if she is to reveal her secrets.

It is always interesting to know the opinions of successful men on such matters, and Mr. Filene, an American business magnate, writes in his book, "The Way Out," as follows:

"This period will ultimately witness a ruthless weeding out of 'the businesses that do not go beyond mere price cutting and 'wage slashing. The survivors will be the businesses in which 'waste has been conquered and scientific method introduced."

Again the American wood alcohol industry has recently suffered a severe check as the result of a new scientific discovery, and in commenting on the fact a celebrated American professor of chemistry says:

"American manufacturers have failed, on the whole, to under-'stand the need for research to keep their industries at the front. 'The backwardness of the manufacturer in this respect only reflects 'that of the general public in this country. The principal trouble 'here, in comparison with Germany, France, and England, is that 'we do not appreciate to the same extent the significance of science 'to the present day civilisation. . . . The whole thing will have its 'value if it is appreciated by American manufacturers and the 'public, as an object lesson of our backward-looking attitude 'towards research."

This writer is evidently of opinion that the general appreciation of the importance of research is greater in this country than in America. Although I have no personal knowledge of America, I do not think this can be possible, nor does the writer in the *Round Table* who, in comparing the trade possibilities of this country and America, points to many of the immense initial trade advantages

possessed by America, and then adds: "If, in addition, they obtain a lead in the application of science to industry it is difficult to see how we can hope to compete with them."

It is not only research that is needed in this country, but research on well-ordered and organised lines. If the suggestion made at the first meeting of the British Association had been carried into effect it is probable that the general appreciation of the importance of science in this country would now have been widespread: but as it is, research has been allowed to be carried out by the individual on his own lines and in accordance with his own fancies, without in any way attempting to produce organised effort for the general welfare of the nation; and the pure research worker has been left to himself to become "a member of a priesthood which prides itself on its detachment from worldly things, a priesthood which refuses admission to any who bear the taint of hope of material gain."

Yet despite this splendid isolation of the pure research worker, what a glorious record of important discoveries is his and how much his country might have benefited if some few of them had been put to industrial use here, instead of becoming milestones in the development of foreign industrial capacity.

It was not until 1914 that any real attempt was made to organise the scientific workers of this country, with what results everyone knows and we have to thank some unknown persons whose ideas led, in July, 1915, to the establishment of an Advisory Council to make recommendations and proposals for:

I. Instituting specific researches.

II. Establishing or developing special institutions or departments of existing institutions for the scientific study of problems affecting particular industries and trades.

III. The establishment and award of Research Studentships and Fellowships.

From this suggestion has developed the Government Department of Scientific and Industrial Research, which in the short time it has existed has done more for the organisation of scientific effort than has ever before been done in this country.

Professor Wynne in his Presidential Address last year spoke in no uncertain terms of the benefit which had accrued to research students as the result of research grants made by the Department, and I need not refer further to item III above. Those who are interested in the other activities of the Department will do well to study somewhat carefully its annual report for the year 1924—1925. Under item I above are included such important problems

as researches connected with fuel, building materials, illumination, adhesives, forest products, foods and cold storage, and many others which have been initiated as a result of co-ordination of research in Government Departments by a series of co-ordinating Research Boards. And under item II come the National Physical Laboratory, the newly-established Chemical Laboratory, the Geological Survey and Museum of Practical Geology, the British Museum Laboratory and Industrial Research Associations.

Many of the difficulties of applying science to an industry as a whole were evidently fully appreciated by the Committee of the Privy Council, and under the title "Impediments to Industrial Research" the following words appear in the Report of the Committee for 1915—1916 *:

"Our experience up to the present leads us indeed to think 'that the small scale on which most British industrial firms have 'been planned is one of the principal impediments in the way of 'the organisation of research, with a view to the conduct of those 'long and complicated investigations which are necessary for the 'solution of the fundamental problems lying at the basis of our 'staple industries. What, for instance, is the exact nature and 'constitution of the cotton fibre, of rubber or of the resins? How 'does the structure of an alloy depend on its chemical composition 'and on its mechanical and heat treatment? . . . These are ques-'tions which none but the greatest of individual firms or a big 'combination of firms could venture to attack."

Yet the initial difficulties seem to have been overcome with great skill and Research Associations have been formed by specific industries, on the principle that the Department would provide money in definite proportion to the amount raised by the industry and would continue these grants for five years. In the case of the cotton industry, the subscriptions from the trade are regulated by the number of spindles or looms in a mill or by the declared capital of the company, and are on a unit principle. Since nearly 90 per cent. of all the firms in the industry are members of the Research Association, and also owing largely to generous help which has been afforded by the Cotton Trade War Memorial Fund Committee, the annual income of this Association is for the next four years approximately £54,000. It has therefore been possible to establish laboratories wherein "the fundamental problems lying at the basis" of the industry can be attacked, for which purpose organised and co-operative research is absolutely necessary. It is true that there are many purely botanical, chemical, or physical

* Report of the Committee of the Privy Council for Scientific and Industrial Research for the year 1915–16, page 25.

problems to be solved, but fundamental research directed towards the general advancement of this industry more often than not means the close co-operative efforts of botanist, chemist, and physicist, and where results are forthcoming, further co-operation with technical men and practical works experience become essential.

Undoubtedly, organised research has been carried on in the past by some firms or industries—the results achieved allow us to make this deduction; but the information gained has naturally remained the property of the firms concerned and does not touch the national programme of scientific work. The aim of the Department's scheme is to advance the industry as a whole.

The grants made by the Department were originally for five years, in which time it was hoped that the Associations would have done so much for their trades that further Government help would not be necessary. But the First Report of the Committee of the Privy Council (page 30) contains these words: "The shortest period in which any considerable results can be expected is five years, while results so considerable as to affect the whole industry cannot be looked for in less than ten years' consecutive work." It has now been proved that five years is too short a time in which firmly to establish such an enterprise, which necessitates the selection of a scientific staff, the building of laboratories, and the collection of a library, together with other research facilities. The British Cotton Industry Research Association was founded in 1920, its laboratories were opened in March, 1922, and it is only now, six years after its creation, that the Association is really getting into intimate contact wth the trade, which is recognising that science is capable of rendering assistance. It may appear to some that progress from the point of view of the trade has been slower than it should have been and it is just possible that more work of immediate use to the trade might have resulted, if those responsible for the foundation of the Association had not decided that the large fundamental problems lying at the basis of the industry were to be the main objects of inquiry. But the founders made a wise decision, for although initial advances may have been slow, future progress will be greatly accelerated by the better understanding of these fundamental problems.

The idea of these Research Associations and the plan on which they have been brought into being seem to me to be the only possibility for the general introduction of science and scientific method into some of our large industries, and the work of the Department in this direction is destined to prove of immense value to the trade of this country, indeed it would not appear too much to say that the whole concept is one of the utmost national importance. The

movement must lead ultimately to greater trade efficiency, to the expansion of trade, and to greater employment both of scientific and industrial workers.

Further, the movement has led to the increase of the number of research workers in laboratories connected with individual firms, and will lead to the larger employment of scientists in works, to establish scientific control, and to form the intelligence departments which will search into the results obtained and endeavour to apply them to industrial progress.

But the Department's scheme has none the less been severely criticised, largely by those who are always willing to pour forth destructive criticism, without attempting to supply anything in the nature of a constructive policy.

Sympathy has often been expressed for me in my supposed efforts to divest my surroundings of Departmental red tape, which, as my well-wishers put it, must stifle any freedom of action relative to research. I can only say that I have not encountered any of this flaming cord. Naturally an Association receiving money from public funds must be required to conform to certain rules and regulations, but these have not been in any way irksome, nor have they in the least interfered with research progress. On the other hand, I am glad to have this opportunity of acknowledging the great help which the Association has received from the Department on all and every occasion on which such help has been sought. One of these aids, which is becoming of increasing importance, is the Department's Information Bureau, which not only serves as a clearing house for research information relative to this country, but is taking on a much wider scope.

It has been frequently urged that it is undesirable, not to say wrong, to devote public money to industrial research, which should be supported entirely by the trade concerned. There is, I think, a very good answer to this criticism. Truly successful research is rarely without benefit to mankind at large and one need not do more to emphasise this point than refer to the life work of such a man as Pasteur. As regards industrial research, it may safely be said that the fruits of such research are always for the public benefit. It has been estimated, for example, that the research work of the General Electric Company of America is saving the American nation at least a billion dollars a year in the matter of electric light.

Those industrialists who found research laboratories with the avowed intention of investigating the fundamental problems of their industries, of ascertaining all there is to be known about the materials which they use, do so perhaps mainly in the hope that

their businesses will thereby be expanded, as the result of the introduction of new or the improvement of old materials and processes. They further realise that this must lead to greater employment, both industrial and scientific, for scientifically controlled production means methodically certain production, with less expense of mental effort and therefore more of the latter for devotion to other work. But they take a chance, for no one can assure them that results of value will be obtained in any stated period. When, however, results are forthcoming, the public, which has staked nothing, gets the benefit every time, whether it be in the way of electric light, artificial silk garments, or more skilful medical treatment. Why, then, should not the public contribute to the cost of research from the results of which they benefit so largely?

But no matter how much criticism is levelled at the Department of Scientific and Industrial Research, it still remains a fact that its activities have led to an organised effort to bring science and industry together, an effort which has already been crowned with distinct success and will lead to a great future, if all those interested will look at the movement in the true national spirit and do what they can to support and further it. For in reality it is a distinct step towards the organisation of the immense research power of this country.

If, however, the results of research are to be effectively applied, it is absolutely necessary that industry should meet science at least half-way. It is useless for the industrialist to complain that he does not understand scientific papers and that they must be put into everyday language, so that he *can* understand them. It is not to be expected that every industrialist can be a trained scientist, but he can at least guard himself by employing trained scientists in his business, thus establishing the position of the man of scientific training in industrial management. The position could not be more clearly stated than in the following words of the Prime Minister, when speaking in the House of Commons in the summer of 1925:

"No one will assert that British industry can be saved by science 'alone, but it is none the less true that until scientific methods 'and scientific men can take their place in industry and an equal 'place with the administrator and the financier, British trade will 'never be strong enough or resilient enough to meet the shocks 'that it is bound to meet as the years go by, or to meet the sudden 'and unexpected changes which will always arise in international 'trade."

Reference has just been made to the immense research power possessed by this country. Are there not other ways in which this power can be put to the nation's benefit? Cannot we so organise

ourselves that at all events some portion of this vast research force is utilised in the solution of some of the problems which are vital for our welfare? In foreign countries much of the research energy of the Universities and higher Technical Institutions is directed by the Professor, himself in the closest contact with the heads of some great industry, towards the solving of important technical problems. Immediate solution is not looked for, but gradually a mass of new information is forthcoming, which in very many cases has led to results of the greatest importance, in regard to the elimination of waste, the utilisation of what have been regarded up to the time as waste products, and the discovery of new materials of commercial value. Frequently this means that a young scientist is sent into a works to watch his laboratory experiments gradually translated into manufacturing possibilities and hence the Professor and also the works authorities have opportunity of judging in which direction his future capacity lies, whether solely for pure research or for the application of science to works problems, etc.

Could not funds be found from somewhere to provide for the training in research method of those who are willing to undertake work on one of the many urgent national problems?

Cannot facilities be provided for sending trained men of science at an early point in their industrial career, to study the industrial methods of other countries?

Neither science alone nor industry alone can set any such ideas in motion, it is only by the honest and hearty co-operation of both sides that any success will be gained.

Is there any amongst us who can truthfully say, These are matters which do not interest or affect me and towards the solution of which I can add nothing of value? Surely, as a result of the simple fact with which I opened my remarks, we are all, without exception and no matter what our every-day work is, ultimately dependent for our existence on the success of our great industries, and although there may be some slight indication of trade improvement, the present situation is sufficiently serious to warrant every thinking man making it the principal national thought for the time being.

Someone has said that the Britisher is a confirmed individualist, from which fact his failures and his successes have arisen; but is it not time that we brought ourselves to realise that there is much unselfish and co-operative national work to be done? The never-ending search for new knowledge is the exacting price which must be paid for survival under modern industrial conditions.

There is another important aspect of the situation which I should like to consider for a few moments: as a teacher, or at all events one who, if not active at the present, has spent a large portion of

his life in the teaching of chemistry, I would ask if we are satisfied that we are doing all in our power to train up a body of young chemists, who will be able to fill the openings which industrial life offers and will in future offer always in increasing numbers, provided we continue to progress. I have given much consideration to this question, especially during the past six years, and I am bound to say that I do not think a wholly positive answer can be returned to the question. One often hears it urged as a serious fault of British manufacturers trading in foreign markets that they supply goods which they "think should be required" by the said markets without troubling to ascertain whether the purchasers have any tastes, desires, or special requirements of their own or whether their natural surroundings render desirable modification of goods made for this country, whereas our competitors do make the necessary inquiries and are constantly reaping the benefit. I rather think the same accusation might legitimately be brought against the teachers of chemistry in this country, who might be considered to be providing chemists who have had the training which the teachers "think should be required" by industry, without troubling to inquire whether industry has any special needs of its own, whether industrial surroundings demand special consideration, or whether one industry differs in its requirements from another. It is granted that such inquiries would demand more than a bowing acquaintance with any special industry. Is it not, however, the duty of the teacher to make such inquiries as equally, in my opinion, it is the duty of the industrialist to make known his requirements to the teaching profession?

It needs but little consideration of the question to reveal the fact that industry requires chemists with broadly differing lines of training, according to the special branch they are going to take up. To my mind, our present training is much too stereotyped, leading to the production of one type of man only. The system produces many extraordinarily good men of this type, but it leaves out of consideration the fact that there are many differing types of men who are not all capable of showing their best qualities as a result of one set method of training.

Take, for example, the industry with which I am connected, namely, the cotton industry; here the chemist has to deal with a biological entity, and if he has not had a training in some biological subject and cannot think from the biological standpoint, much of his time and of his employers' time will be wasted, for it is hopeless to look upon the cotton hair as a definite "substance" from the chemist's point of view.

Among the various types of chemists required by industry is

the research worker pure and simple, who will be free to devote his abilities solely to the advancement of knowledge and who need not of necessity have any business qualifications or adaptability for applying his knowledge to industrial problems. He may be the true specialist in some branch of his science.

A second type of chemist, quite as rare as the true research worker, quite as important in industry, and yet possessing an entirely different outlook of mind, is the man who can apply new scientific data to industrial development and can convert laboratory experiments into industrial operations. Then there is the process chemist, whose duty is not the furtherance of abstract knowledge, but the careful scientific control of works processes. He again is a most important type, for there are few industries in which better technical results could not be obtained by more careful scientific control. One of the main requirements from such a man is his capacity to do, or to supervise, accurate analytical work, requiring frequently a high order of attainment as an analyst, a qualification not always demanded by our present examination system. As a fourth type may be mentioned the chemical engineer, probably more wanted in this country than any of the other types.

Now, are we doing our best for our future chemists or for industry by putting them all, together with future school and university teachers, through the same courses of study? Personally I do not think that we are. I shall probably be met by the criticism that there is only one chemistry and therefore there can be but one way of teaching it. Here I disagree, because I feel that the present system leads to the production of narrow specialists, who have not a wide outlook on science generally. In most chemistry schools, especially those of the newer universities, the Honours chemistry course extends over three years, and although classes in physics and mathematics may be a part of the curriculum, this does not of necessity imply any real absorption of these sciences. I am a firm believer in a broad general training in, say, three sciences before the student proceeds to specialise in any one of them; the system, in fact, which used to prevail in the University of London and is still in vogue in a few of our Universities.

Moreover, I do not think the present method of examination is giving us the desired information about candidates or is enabling them to realise what is before them in the future. Far too much is expected from them in the way of book work and far too little in the way of accurate straightforward chemical manipulative skill. Here is what a friend wrote to me the other day, when calling my attention to a really capable young chemist: "My recommendation

is only based upon the possibility of your happening to need a pair of well-trained and capable hands, backed by a mind that is naturally endowed with the scientific curiosity which leads to research. I dare say that, like myself, you have often found that sound scientific training and even brilliant chemical knowledge is sometimes acquired in a University, without the acquisition of any ability to use the hands for sound accurate quantitative work, partly because in some of the University laboratories the value of manipulative skill is not appreciated, and partly because nowadays such an immense amount of theoretical work has to be crowded into the college course that there is little time for the humble utilitarianism of routine analytical operations, though the accurate acquisition of facts is not less important than the projection and co-ordination of the inquiry on which they bear."

I agree with these sentiments entirely and can say with certainty that much has been done to make industry sceptical of the value of trained chemists by the fact that Universities have sent out into the world as first class honours graduates men who could write reams on ill-digested facts concerning molecules, atoms, and subatoms, but who had no competency whatever for conducting a straightforward piece of ordinary analytical work. By all means let us give our students a good theoretical grounding and, provided this foundation is sound and on broad lines, the good men will be able to build for themselves upon it, in accordance with the necessities of their future occupations.

I could not attempt to trace here the training that a chemical engineer should be put through, but I do think that everyone going into industry should at all events have some slight knowledge of the subject. Might it not reasonably be made a third subject for a pass degree ? I do not by this mean to imply that such a training would be adequate for anyone who wished to become a full-fledged chemical engineer, but it would at all events help a young man going into industry to bridge over the chasm, which exists at present, between the laboratory and works operations. I have often seen a look of astonishment and blank dismay come over the face of a young chemist when he has been shown for the first time a working drawing of a piece of chemical plant. There is certainly no reason why every future industrial chemist should not be taught sufficient of machine drawing and design to enable him to read these drawings with ease.

It must, of course, be granted that there is much, very much, concerning industrial chemistry which cannot be taught in University laboratories and can only be learnt in the works itself, but I think it should be possible, with more co-operation between industrialists

and teachers, to make the learning considerably easier than it is at present.

If it be admitted that our training of future industrial chemists is not all that could be desired, can the blame for this state of things be placed on the teachers only? This question can undoubtedly be answered by an unqualified negative, and others may be asked, for example, What have industrialists done to co-operate with the teaching profession in the training of young chemists? Have industrialists offered any slight advantages to students during their training, or have they in any way made clear their wants, and have they helped as far as possible in making their wants practical possibilities? It would appear that little has been done in any of these directions, and the idea is still prevalent among many industrialists that "the young man who grows up with the business will acquire all the knowledge he needs."

In these circumstances it is an encouraging pleasure to record the fact that the Managing Director of the British Dyestuffs Corporation forwarded in July, 1925, for the information of your President, a copy of a letter which had been addressed to Professors at the various Universities, pointing out that the progress of the synthetic organic chemical industry in Britain depends so largely on the achievements of British chemists, both within and without the industry, and is a matter of such national importance that the most sympathetic co-operation is necessary between the Universities, Technical Schools, and the industry. The letter then invites co-operation in several ways, such as advising the Corporation of likely students for research departments or works processes; giving early notice of laboratory researches likely to have an industrial application; allowing students to carry out researches in conjunction with the Corporation, etc. Finally came the information that the question of permitting a limited number of students to gain works experience with the Corporation during the long vacation was receiving sympathetic consideration, so sympathetic, in fact, that the suggestion materialised and I believe some fifteen students were given, during the summer vacation of 1925, the opportunity of acquiring knowledge in the works of the British Dyestuffs Corporation. The result from the students' point of view was an unqualified success and can scarcely have been a failure from the point of view of the Corporation, since this body is again granting similar facilities to students this summer. The warm thanks of all interested in the training of industrial chemists may be given to the Corporation for this example of the co-operation which is so greatly needed, and for so definitely disproving what in the past was frequently stated to be an impossibility, owing to the dis-

organisation of works practice that it would cause, and also to the danger of works secrets leaking out. If such difficulties have arisen in the present case, it is obvious that the Corporation is willing to face them in view of the importance of the whole question.

In his address last year Professor Wynne directed attention to the desirability of such experience being made possible for students, and stated that in Sheffield the problem had been faced and solved, since it is now the custom for intending graduates in Metallurgy to spend part of the long vacation in certain of the steel works in Sheffield, to be welcomed there and to be placed under foremen to do such work as may be suggested. Now we have the proof that such a state of affairs is not an impossibility in chemical works, and it is to be hoped that the important example set by the British Dyestuffs Corporation will be largely followed by other firms.

Much has been heard recently of the necessity of co-operation between employer and employed, but there is at least as much need for co-operation between business men and teaching institutions regarding educational matters. No one can afford in the interest of our national welfare to say that he has no interests in education, for it is an essential part of the life-work of everyone.

This nation possesses, in addition to others, two most powerful assets which individually have reached great heights. I refer to practical industrial experience and scientific research capacity. If these two forces can be linked together, if the exponents of each can be brought into intimate contact and will in every way possible heartily co-operate with one another, then there is no reason to be pessimistic about the future, for the possibilities such a co-operation opens out are unlimited.

And now, in conclusion, I would express to the Officers, Council, and Fellows of the Society my great appreciation of their kindness to me during my term of office and my deep regret that I have not been able to complete the usual period of two years. I can only say that my interest in the Society has not waned and that I hope in the future to be able still to be of service to the Society.

I should like to add a very special word of thanks to the permanent officials of the Society with whom I have now worked uninterruptedly for 21 years: to Mr. Carr and to Mr. Clifford my sincere thanks are due for the willing and pleasurable way in which they have co-operated with me: and I should also like to thank Sergeant Holland for the share which he has taken in helping me with the work of the Society.

OBITUARY NOTICES.

JOHN YOUNG BUCHANAN *

BORN FEBRUARY 20TH, 1844; DIED OCTOBER 16TH, 1925.

JOHN YOUNG BUCHANAN was born in Glasgow on February 20th, 1844. He was the second son of Mr. John Buchanan of Dowanhill and the elder brother of the Right Hon. T. R. Buchanan, M.P., who represented Edinburgh in Parliament for many years. He was educated at the Glasgow High School and the University of Glasgow, where he graduated in Arts in 1863. His attention had been turned to Chemistry, and he proceeded to study this science on the Continent, spending several years in Germany at the Universities of Marburg, Bonn, and Leipzig, and going on in 1867 to Paris, where he worked in the laboratory of Würtz, a master for whose scientific genius and personal kindness he always cherished a warm admiration.

Shortly after his return to Scotland Buchanan was appointed Assistant to Professor Crum Brown, then recently established in the Chair of Chemistry in the University of Edinburgh, and in 1870, on Crum Brown's nomination, he was elected a Fellow of the Royal Society of Edinburgh.

When the voyage of H.M.S. *Challenger* was planned for the purpose of investigating the physical and biological conditions of the great ocean basins, it was decided that one representative of the physical sciences should be charged with all matters concerning physics, chemistry, and geology, except such hydrographical and meteorological observations as had been assigned to the naval officers. Buchanan was chosen for this comprehensive post by the Circumnavigation Committee of the Royal Society, who had prepared the programme of scientific work. His selection was due largely to his skill and resourcefulness in devising and making apparatus, his reputation as a practical chemist, his knowledge of mineralogy, and his interest in all natural phenomena. The wisdom of the choice was fully justified. Five years were entirely occupied by the *Challenger* work; the preparations for the cruise, and the fitting up of a chemical laboratory in the small space available on board, taking up several months before the ship sailed in December 1872, and the completion of work in hand occupying a longer time after the ship returned in June 1876.

Throughout those years Buchanan's mind was bent on the practical

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problems arising in the study of sea-water; but he took full advantage of the many opportunities for excursions into little-known lands when the ship was in port, and he acquired a love of travel that never left him.

He returned to Edinburgh and set up a private laboratory, in which he carried on research on his own account. The possession of ample means made it unnecessary for him to seek any professional appointment, and he continued to spend much of his time at sea. He made investigations on the west coast of Scotland and on the lochs of the Great Glen in his steam yacht, the *Mallard*; and he took part in several voyages of the cable-laying ships of the Silvertown Company on the west coast of Africa and across the Atlantic, mastering the new methods of sounding by wire, which superseded the clumsy processes of the *Challenger*.

In Edinburgh he entered into the remarkable revival in the study of physical geography and kindred sciences which was a feature of the eighth decade of the nineteenth century, and he took a share in establishing the Ben Nevis Observatory, the Scottish Geographical Society, and the Scottish Marine Station. He contributed a large quantity of material for the equipment of the Physical and Chemical laboratory of the original Marine Station at Granton in 1884, and the writer of this notice had many opportunities there of profiting by his instruction in the arts of observing and recording. In 1887 the Royal Society of Edinburgh awarded the Keith Prize to Buchanan for his work in chemical oceanography, and in London the Royal Society elected him a Fellow.

Buchanan was on terms of friendship with Professor Robertson Smith, who encouraged him in the study of physical geography, and helped to persuade him to accept the lectureship in Geography in the University of Cambridge in 1889. Buchanan was given the Cambridge degree of M.A., and took rooms in Christ's College, where Robertson Smith was already established. He resigned the lectureship after holding it for four years, but Christ's College continued to be his home for twenty years, and in his will he left substantial proof of the regard he entertained for it. On leaving Cambridge, Buchanan took up house in London; but he was much abroad, frequently visiting South America, where he had property in the Argentine, and staying at continental resorts, where he had many friends, some of them in very high positions. Kindred tastes cemented a close friendship with Prince Albert I. of Monaco, and he spent much time as the Prince's guest on shore and afloat, making many cruises in the Mediterranean, the Atlantic, and to Spitsbergen in the Prince's yachts, which were splendidly equipped for oceanographical research.

The outbreak of war in 1914 was a blow from which Buchanan never recovered. He had been on terms of personal friendship with the Kaiser and other distinguished Germans, while his old scientific associations with France had been strengthened by his membership of the governing body of the Oceanographical Institute, founded by the Prince of Monaco in Paris. In real distress of mind, Buchanan gave up his London house and betook himself to Havana, in the West Indies, until hostilities ceased.

His last work was the preparation of three volumes, published by the Cambridge University Press, containing reprints of those of his papers which appeared to him the most worthy of preservation. To these he prefixed very copious analytical Tables of Contents, with comments and criticisms often of great interest. The volumes were: *Scientific Papers*, vol. i.—*Oceanographical*, published in 1913; *Comptes Rendus of Observation and Reasoning*, in 1917; and *Accounts Rendered of Work Done and Things Seen*, in 1919.

After his return to London in broken health, the isolating shadow of old age fell on him, and he withdrew more and more from the society of his remaining scientific friends. He died at the age of eighty-one, on October 16th, 1925.

Buchanan's scientific work was directed to the elucidation of practical problems presented to him during the voyage of the *Challenger*. He did not care for theoretical deductions or comprehensive generalisations. He seemed to work mainly for the satisfaction of his own mind, for once a definite result was obtained the problem lost its driving power; and only a portion of the notes which he amassed, with a care and precision that can only be described as meticulous, was ever worked up for publication. He used to say that he loved work but hated writing; still, the number of his published papers exceeds one hundred.

On the *Challenger* most of his time was filled by a routine prescribed by the Circumnavigation Committee, but the tedium was lightened by flashes of discovery. One was the fact of large concretionary deposits of manganese peroxide produced by chemical action of sea-water on minerals. Another was the discovery that the gelatinous substance found on all preserved deep-sea deposits, which Huxley had taken for a primeval organism and named *Bathybius Haeckeli*, was really a precipitate of calcium sulphate thrown down from sea-water by the addition of alcohol.

The short stay of the *Challenger* in Antarctic waters raised the question of the formation and melting of sea ice, on which Buchanan worked with great keenness for several years, producing a series of valuable papers on "Ice and Brines," in which he worked out the chemical and thermal changes accompanying the freezing of saline

solutions and the temperature at which pure ice melted in them. This led to a further series of calorimetric researches on "Steam and Brines."

Another subject raised on the *Challenger* and settled in a shore laboratory, was the compressibility of glass and other substances under the pressure of the deep sea, ranging up to 5 or 6 tons per square inch. The apparatus invented for this purpose was handed over to Professor P. G. Tait, and used by him in determining the pressure corrections of the *Challenger* thermometers.

Buchanan's most important contribution to the *Challenger* Reports was a memoir on the "Salinity of Ocean Water," in which he published the first complete map of the world-wide distribution of surface salinity, the main features of which have been fully confirmed by later investigators.

His work on the Telegraph ships resulted in a study of continental slopes and oceanic shoals, which had scientific as well as practical value. One of his few general papers was a suggestive survey of Similarities in the Physical Geography of the Great Oceans, contributed to the Royal Geographical Society in 1886. In Limnology he was the first to prove that vertical circulation set up by the wind produced a winter temperature of the deep water in a lake far below the maximum density point.

The work of Buchanan was that of a pioneer breaking new ground, and it was his fate, which he recognised and perhaps resented, to make observations of fundamental importance, which were lost sight of under the superstructure raised by others whose names are better known to the scientific public. All he did was original work in the fullest sense. He owed nothing to other workers. He insisted always on going to the fountain-head, preferably by direct observation, for all data, and on handling such data in the way most likely to ascertain their true relationships even if that required difference from recognised authorities.

His character exhibited singular sincerity, and a kindliness which he did nothing to advertise. Although to acquaintances his manner may often have seemed cold and distant, his nature showed a very warm and friendly side to the few congenial comrades of his choice.

H. R. M.

GIACOMO LUIGI CIAMICIAN.*

BORN AUGUST 27TH, 1857; DIED JANUARY 2ND, 1922.

GIACOMO LUIGI CIAMICIAN was the son of Giacomo Ciamician and Carolina Ghezzo and was born at Trieste, where his father's family,

* Translated by Sir Wm. J. Pope.

J. Clemenceau

[*To face p.* 996.]

of Armenian origin, had not been long established. The family claimed descent from the great 18th-century historian of the Armenian people, Michele Ciamician.

Ciamician received his secondary education in his native Trieste, where Prof. Augusto Vierthaler initiated him into chemistry; he then studied at the Polytechnic and the University of Vienna, devoting himself principally to Chemistry under Professors Barth and Weidel. While still a student he busied himself enthusiastically and with no little insight upon biological and physical investigations and published several papers of importance, thus laying the foundation of that broad appreciation of physical and biological science which became so evident in his later scientific work and which set the stamp of character on his future triumphs. In 1880 he became a Doctor in Philosophy in the University of Giessen and in the same year was appointed assistant under Stanislao Cannizzaro in the Institute of General Chemistry of the University of Rome. While in Rome, where he remained until 1887, he was appointed to a Readership, and in this capacity delivered, first, courses of lectures on spectroscopy and, later, on the nitrogenous organic compounds. In 1887 he was chosen in competition for the post of Professor of General Chemistry in the University of Padua, and in 1889, again competitively, he was elected into the corresponding chair in the University of Bologna; here he remained until his death, giving two courses, those of general and inorganic chemistry and of organic and biological chemistry.

The scientific work of Ciamician can be classified in six large groups:

1. *Various Chemical and Physical Investigations carried out between* 1877 *and* 1880.

This group comprises ten memoirs which deal particularly with spectrum analysis, and also with the resins and the composition of Dippel's oil; it treats of work done in the Polytechnic and the University of Vienna before its author proceeded to his Doctor's degree. The contributions to spectroscopy are of the greatest interest, presenting as they do a comparative study of the spectra of homologous elements which belong to the same group in the periodic system. Ciamician foresaw much that has been since firmly established by more modern methods; he affirmed the spectroscope to be the instrument destined to elicit information concerning atomic motion, and declared that analogous elements of the natural system have analogous structures. These conclusions were far in advance of their time, and it is small wonder that even Mendeléev and Wm. Ostwald judged them as fanciful.

2. *The Study of Pyrrole and Allied Compounds.*

This group includes about eighty papers published between 1880 and 1905; therein are described many derivatives of pyrrole with the details which establish the chemical character and behaviour of this base. The aromatic nature of pyrrole and its analogies with the phenols are here developed; these are questions of prime importance in connexion with this group of compounds and later became fundamental to the study of chlorophyll and hæmatin. The reduction products of pyrrole, pyrrolylene, and more especially of pyrrolidine, prepared for the first time in 1885, call for particular mention in that these groupings form part of the nuclei of such important alkaloids as hygrine, nicotine, cocaine and atropine, and of the proteins.

The results of these investigations were collected in a monograph "Il Pirrolo e i suoi Derivati," published in 1888, which gained for its author the Royal Prize of the Accademia dei Lincei. Ciamician gave a masterly review of the whole subject in an address to the Deutschen Chemischen Gesellschaft "On the Development of the Chemistry of Pyrrole during the last Quarter of a Century," in 1904 (*Ber.*, 1904, **37**, 4200). Amongst the work done in this field should be noted the discovery and utilisation of tetraiodopyrrole or *iodol*, which has found considerable therapeutic use as a substitute for iodoform. To be remarked also is the preparation from pyrrolidine of butadiene, a hydrocarbon which later became so important in connexion with the synthetic manufacture of indiarubber. Meyer and Jacobsen ("Lehrbuch der organischen Chemie," 1920, **2**, 147) refer to this group of investigations in their statement—"Das eigenartige Verhalten der Pyrrol-Körper wurde besonders durch eine grosse Reihe von trefflichen Untersuchungen beleuchtet, welche man dem italienischen Forscher Ciamician und seinen Schülern verdankt."

3. *Researches on Certain Vegetable Components.*

Thirty-seven papers are devoted to this subject and appeared between 1888 and 1899. The constitutions of a number of organic compounds of vegetable origin were established by these investigations. The work on apiole, and the conversion of safrole and eugenol into their isomerides, which was vital to the industrial manufacture of heliotropin and vanillin, here call for mention; so also does the study of the components of the Coto and similar barks, of pseudopelletierine and the constituents of the essential oil of celery, in which the constitution of the aromatic principle, sedanolid, was elucidated. This was one of Ciamician's finest pieces of work; it

preceded that of Willstätter, who developed with such success, and in a variety of directions, the line of investigation so well marked out and defined by Ciamician.

4. *Researches on the Chemical Action of Light.*

Forty notes and nine memoirs were published between 1900 and 1915 on this subject, which was developed into the first systematic study of the behaviour of organic substances towards light.

These researches on the action of light were initiated by Ciamician at Rome in 1886 by his investigation "On the conversion of quinone into quinol by light" and "On the action of light on nitrobenzene in alcoholic solution." They were resumed actively in 1900 and carried on until 1915 in conjunction with Dr. Paolo Silber, who had collaborated in most of Ciamician's work since 1882. The war interrupted this partnership, which is one of the longest, the most fruitful, and the most disinterested joint efforts in chemical scientific investigation. In the course of this work the following photochemical reactions were discovered: the reciprocal reduction and oxidation of alcohols and carbonylic compounds such as aldehydes and ketones, the reduction of aromatic nitro-derivatives by alcohols and aldehydes, the polymerisation of unsaturated compounds and their isomeric changes—this was extended also to the oximes—the hydrolysis of open- and closed-chain ketones, and also of *cyclo*hexanone and its derivatives, of menthone, of camphor, and of fenchone, the condensation of hydrogen cyanide with ketones and aldehydes, the aldol condensation of alcohols and ketones, and the synthesis and autoxidation of γ-diketones.

The earlier portions of this series of studies were summarised in a brilliant lecture "On the Chemical Action of Light," delivered before the French Chemical Society in 1908. The later publications on photochemistry treat of the autoxidation of organic acids and of ketones, of bases such as piperidine and nicotine, and of the reduction of copper salts by acetic and benzoic aldehydes. As of especial interest in connexion with autoxidation may be noted that of the *cyclo*hexanones, which yield dicarboxylic acids and the corresponding ketones by opening of the ring, and that of oleic acid, in which the double bond is broken, giving a series of lower fatty acids and providing an explanation of the occurrence of rancidity.

During his researches on light as a chemical agent, Ciamician acquired the conviction that the future of organic chemistry lay in its application to biological chemistry and that the more the chemist makes his methods approximate to those of natural pro-

cesses the better he will succeed in elucidating the secrets of nature. Ciamician was never interested in making new compounds for their own sake; he held in horror those substances which only figure in Beilstein, and his work followed no fashion, but was always directed towards the solution of fundamental problems. Plotnikov, impressed by the mass of work carried out by Ciamician and Silber since 1900, has stated that this year marks the basic date in the history of photochemistry.

5. *Researches on Vegetable Chemistry.*

This group of studies is described in nine notes and twelve memoirs and was initiated by Ciamician in 1908 in collaboration with his assistant, Dr. Ciro Ravenna, now Professor of Agricultural Chemistry at Pisa, and was continued until a few months before his death. The problem involved was that of the origin and the functions of the vegetable glucosides and alkaloids.

These investigations constitute a broad and happy attempt to elucidate the functions and mutual transformations of the substances contained in the living plant; its most valuable result has been the synthesis of glucosides by introducing the aromatic compounds concerned into the plant. Thus, salicin is formed as a result of inoculating growing maize with salicyl alcohol. Further, on introducing nitrogenous substances, and especially amino-acids, into plants which produce alkaloids, the production of the latter is increased: thus, asparagine increases the formation of nicotine in the tobacco plant. In another series of experiments, the influence of certain organic substances on the germination and development of plants was studied with a view to ascertaining the function of the alkaloids. From all this work it appears to be indicated that such accessory products as alkaloids, produced in the living plant, are not excretionary products, but exercise a function which may be similar to that of the hormones in animals.

Ciamician summarised his work and its conclusions in an elegant and lucid address "On the Biological Significance of Alkaloids in Plants," delivered in October, 1921, at the meeting in Trieste of the Italian Association for the Advancement of Science. This was the last occasion on which he spoke in public, and he concluded the account of this very beautiful piece of synthetic work by stating—"The conclusion deduced from what we know at present, is that the plant practises a chemistry corresponding to that practised in the laboratory, but does so by means infinitely more simple than ours, although with objects similar to ours. The plant organisation is less differentiated than that of animals, and volitionary manifestation is less developed, but amends are made

by the exercise of a highly perfected chemical technique; the plant consciousness is a chemical consciousness."

6. *Memoirs and Notes on Physical Chemistry.—Addresses and General Discourses.*

The first work of Giacomo Ciamician was on physical chemistry, and he continually followed the development of this science; indeed, he made notable contributions to it by a few but fundamental papers. The note "On a Lecture Experiment for Demonstrating Raoult's Law," and that "On the Theory of Electrolytic Dissociation," in which he was perhaps the first to advance the idea of complexes formed between the ions and the molecules of the solvent (*i.e.*, solvates of the ions), are worthy of remark. Again, the paper "On the Relations between the Chemical Constitution and the Property of forming Solid Solutions of Organic Compounds" was the starting point of fruitful investigations in his own laboratory and culminated in the classical work of Bruni on solid solutions. The note on "Considerations on the Nature of Chemical Affinity and of the Valency of the Atoms," published with Padoa in 1918, came early in the introduction into our science of the electronic constitution of the atom, and some of the views put forward are really profound and merit further development now that the secrets of atomic constitution seem in the main unveiled. Ciamician's point of view in the treatment of questions of general interest was a very admirable one. In his inaugural address on "Chemical Problems of the New Century" in 1903 he showed a real gift for the dignified but at the same time efficient popularisation of science; this power was still further developed in a lecture on "Problems and Objects of Modern Organic Chemistry," given at Vienna in 1907, in those on "Organic Chemistry in Organisms" at Parma in 1908, and on "The Co-operation of the Sciences" at Naples in 1910, and, lastly, in his magnificent discourse on "The Photochemistry of the Future," read at New York in 1912 before the 8th International Congress of Applied Chemistry. In this sparkling address he developed many fundamental conceptions which have been taken up in numerous later well-known utterances by others; he insisted on the need for setting plants to work, so that we may conserve, so far as may be possible, our natural wealth of fossil fuels, which is really small, and of applying photochemistry in desert regions to the utilisation of the solar radiation.

"On the arid earth," he says, "will spring up industrial colonies without soot and without chimneys: forests of glass tubes and greenhouses of all sizes will rear themselves before the sun, and in this transparent apparatus will proceed those photochemical

processes of which the secret and the monopoly are at present held alone by the plant, but which human industry will learn how to wrest from it. That knowledge will be usefully applied in quite new ways, because whilst nature is incapable of haste, humanity can act more speedily; if, in some distant future, the moment arrives when fossil carbon becomes exhausted, it will not entail the death of civilisation, for life and its amenities will endure so long as the sun shines." He took up this argument again, and in a form which appealed to a larger public, in his article on "Chemical Industry without Carbon," published in the "Nuova Antologia" in 1917.

Amongst other writings of Ciamician which call for special mention are those devoted to the memory of Stanislao Cannizzaro and of his intimate friend Augusto Piccini, and the discourse, pregnant with thought, delivered at the celebration of the 70th birthday of Guglielmo Koerner.

The vast output of scientific work of outstanding merit produced by Giacomo Ciamician has been very briefly summarised in the above pages; it appears the more remarkable by contrast with the penury of his laboratory, which made his work a real struggle. He was an incomparable master in the laboratory and the lecture theatre and a great stimulus to energetic work. His numerous pupils now fill the most important chairs of chemistry in Italy and hold high the renown of Italian chemistry; amongst them may be mentioned Angeli, Magnanini, Plancher, Garelli, Bruni, Mascarelli, Ravenna, Boeris, Cambi, Barbieri, Padoa, and Ciusa, together with Zanetti and Rimini, who have passed away. He initiated and vigorously inspired much original work which did not come strictly within his own field; thus arose the investigations of Bruni, Garelli, and Padoa. Himself indefatigable, he inspired in all a noble enthusiasm for assiduous work. His lectures, to which he devoted himself like an apostle, were models of elegance, of precision, and of vivacity, as well as in the choice of experiments; they were one of his great passions, and it was always for him a sad day when he could not appear before his class, which welcomed him with growing applause, repeated at the close of the lecture. Against the advice of his friends and students, and when already attacked by fever in November 1921, he wished to commence his courses in general and in organic chemistry; immediately afterwards he was laid aside by the insidious malady which took him from us.

Giacomo Ciamician was a member of practically all the Italian Academies and scientific bodies, as well as of a large number of foreign societies. He had been President of the Italian Society for the Advancement of Science and of the Italian Association for Pure and Applied Chemistry; he was an honorary member of the

English, French, German, and American Chemical Societies, and a foreign member of the French Academy of Sciences. He was an honorary LL.D. of the University of Glasgow and an honorary member of the Royal Institution of Great Britain. He did not seek dignities, but he was a Cavaliere dell' Ordine del Merito civile di Savoia and a Chevalier of the Legion of Honour. After 1910, he worked actively as a member of the Italian Senate. He had a distaste for militant politics, but nevertheless his voice did not fail the Senate when questions arose which concerned education or the chemical industries; his principles were broadly liberal and he was greatly attached to his native Trieste. Immediately after his graduation he left Vienna, although he could have found there an ample career and ample means for carrying out his work, and came to Italy. At the death of Professor Weidel, an occasion offered for his election as Professor in Vienna with honours, means of work, and emoluments far greater than those he enjoyed in Italy; notwithstanding his gratitude to his former teacher, Professor Lieben, he never thought for a moment of abandoning Italy.

During the war he devoted his great abilities with much self-sacrifice but with juvenile enthusiasm to the work allotted to him; this work was arduous and intense and, whilst without doubt valuable to our country, undermined his already shaken constitution. Towards the end of the war he was smitten by two great sorrows, first, the death of his mother and later that of his dearly-loved sister, Carolina, the wife of Professor R. Nasini. The last great pleasure of his life was to witness the liberation of his native Trieste. Trieste had always held him in affection and esteem as one of the elect of her sons, and decided on his death that the Via degli Armeni, in which is the house of his aunts on the mother's side where he passed his youth and which he made his home when in Trieste, should be renamed the "Via Giacomo Ciamician." On the house in which he was born, 21 Via S. Martiri, the Municipality has placed a bronze medallion with his portrait and an inscription by the well-known patriot and scholar, Senator Attilio Hortis.

Ciamician was of a benign and fine presence; his blue eyes expressed his great kindliness and revealed the simplicity of his nature; he was easily moved to anger, but incapable of harbouring offence. He had a genius for friendship and lavished a noble affection upon his intimate associates; he was simple and upright in private life and a model of the civic virtues. His mind was open to all the great modes of intellectual expression; amongst the arts he loved above all that of music, and in this, even in musical Bologna, he was considered as one of the highest authorities. The Queen Margherita held him in affection and enjoyed his thoughtful

and animated conversation; he had friendships amongst all the chief chemists of his day, more particularly with Emil Fischer, who several times proposed him for the Nobel prize, with Albin Haller in France, and with Henry E. Armstrong.

Bologna was proud to look upon him as one of her citizens and followed anxiously the vicissitudes of his last illness, an insidious malady from which so rapid an end was not to be foreseen. He passed away quietly in the arms of his brother-in-law, Professor R. Nasini, and of his nephew, Dr. A. G. Nasini, and surrounded by his relatives from Trieste; most of his former students had collected in Bologna to be present at the end. They took part in the last solemnities when he was laid to rest on a cold and bright January day; to the accompaniment of Beethoven's funeral march, as Ciamician had wished, the great procession passed among the mourning populace through the streets of the old turreted city he had loved so well.

A memorial stone has been placed by his students on the house which he had always occupied, No. 3 Via Guido Reni. In a short time the new Chemical Institute will be inaugurated; Ciamician had devoted much of his activities to this project and its execution and hoped much from its future. It will carry on its façade the inscription "Istituto Chimico Giacomo Ciamician." An honour worthy of the great man of science.

RAFFAELLO NASINI.

SAMUEL HENRY DAVIES.

BORN SEPTEMBER 19TH, 1870; DIED MAY 9TH, 1925.

SAMUEL HENRY DAVIES was born at Liverpool on September 19th, 1870, the son of Richard Davies, pharmacist. He received his early schooling in Liverpool, and was then for four years at the Friends' School at Sidcot in Somerset, where he already showed a keen interest in chemistry. He studied successively at University College, Liverpool, and Owens College, Manchester, and graduated B.Sc. at Manchester in 1890 (M.Sc. in 1893), winning a scholarship which took him to Heidelberg. Here, under the direction of Victor Meyer, he carried out a research on "Alkyl and Acetyl Sulphides," which was published in the *Berichte* in 1892, and a minor research with Emil Feith on the "Action of Hydroxylamine Hydrochloride on Acetomesitylene."

After returning to England Davies held university posts as demonstrator first at Manchester and later at Leeds, and won the esteem of professors and students. His professor at Leeds says: "I never parted with a demonstrator more reluctantly, for

he was an excellent teacher full of life and go, ready to take up and carry out any promising new plans of instruction."

In 1893 Davies was appointed the first head of the chemical department at the new Battersea Polytechnic; into the organisation of this department he threw himself with whole-hearted and characteristic energy. Here he remained until in 1896 he was appointed chemist to Rowntree and Co. at the Cocoa Works, York. This post he held for more than twenty-five years, during which the original small laboratory with one assistant grew under his direction to a finely-equipped department with a staff of fifty.

Davies was a man of the widest human sympathies and his work at York did not end with his duties as chemist but covered a varied field; he lived a very full life both in the works and in the city. He took the keenest possible interest in the welfare of the workers and in their various clubs and social activities, devoting much time in the earlier days to the swimming, rowing, and football clubs.

In 1907 Davies married Miss Edith M. Oliver and about this time was elected a member of the York City Council, on which he represented Castlegate ward for nine years. He was a strenuous advocate of the feeding of necessitous school children and of a clean milk supply and was the author of pamphlets published by the York Health and Housing Reform Association.

Much of Davies's work for the firm could not be made the subject of publications, but in 1904 he published (with McClellan) a paper on the amount of fat contained in cocoa beans of different origin and in 1912 (with J. S. Bainbridge) a valuable paper on "The Essential Oil of Cocoa." He directed much attention to the general problems of factory working, and papers published in 1903—1904 on the "Relative Efficiency of Insulating Media" embody the results of detailed research on the comparative value of materials used for covering steam-pipes. He also wrote on factory ventilation and lighting and devised a simple and rapid method for the estimation of carbon dioxide in the atmosphere.

On behalf of Rowntree and Co. Davies made journeys in many countries, notably in South America and the West Indies; he returned to the West Indies several times in connection with the development of Rowntrees' estates. He always maintained his interest in these islands and was a prime mover in establishing the Technical College in Trinidad, of which he was appointed a governor.

Davies was a member of the Fell and Rock Climbing Club and, an enthusiastic lover of mountains, spent many summer holidays in the Tyrolese Alps.

From 1919 Davies suffered from ill-health and after a break-

down in 1922 relinquished his full time duties at the cocoa works, but was still retained by the firm as consultant. He built himself a new home and a laboratory at Jordans in Buckinghamshire, where he intended to continue research work, but his health broke down completely and he passed away on May 9th, 1925.

Davies possessed an unusual charm of manner and disposition and was beloved by a wide circle of friends; excellent chemist as he was, chemistry was to him but one means of approach to his fellow men. A writer in the *York Gazette* says of him: "When S. H. Davies saw something to be achieved which could bring gladness and essential prosperity into the lives of his neighbours, he sought for this with his whole soul and strength, however strong and influential the forces against him," and one who worked with him in his later years rightly described him as "gentle and charitable, indulgent to others, severe to himself and unwearying in service to friends." His was a noble nature and we who knew him are sorrowful that he has left us so soon.

REGINALD BROWN.

WILLIAM HENRY DEERING.

BORN DECEMBER 19TH, 1848: DIED SEPTEMBER 5TH, 1925.

WILLIAM HENRY DEERING was the youngest son of W. Deering of Gravesend. He received his early education at the City of London School and in 1864 entered the College of Chemistry as a student under Hoffman. After short periods as assistant to Sir Benjamin Brodie at St. Bartholomew's Hospital and with William Odling at Oxford, in 1867 he joined the staff of Sir Frederick Abel, Chemist to the War Department, at the Royal Arsenal, Woolwich. He spent the rest of his life, until his retirement in 1909, in the Government service, becoming himself Chemist to the War Department in 1905.

Like that of many other civil servants, Deering's work was unknown to the general public, but he played no small part in the application of chemical science to military materials which showed so remarkable a development towards the end of last century. Although the introduction of cordite is associated with the name of Sir Frederick Abel, the fundamental researches which led to its adoption in the British Service necessarily depended on his assistants, and of these Deering and his colleague, the late William Kellner, were mainly responsible for the work. It is sufficient testimony to the thoroughness and completeness of their labours that, in spite of continuous efforts to improve upon it, the cordite of to-day is substantially the same as that introduced into the Service in 1889.

In addition to his work on cordite, Deering was called upon, in the course of his long service, to deal with a large variety of chemical and physical problems in connexion with explosives and other military stores. He carried out much important investigation in perfecting electrically-fired detonators for use in the field.

As regards contributions to the literature of their profession, scientific officers of the public service suffer from certain disabilities. It frequently happens that their more important work is of a confidential nature, or, if not, that it is published in the form of a report by the Head of the Department, in which the part played by individuals is not shown. To these facts, coupled with Deering's marked distaste for publicity, is due the relatively small number of papers under his name. Perhaps the most important are those (with Abel) on the conditions in which carbon exists in steel (J., 1883, **43**, 303) and (with Kellner) on the measurement of pressure by the crusher gauge (*Proc. Roy. Soc.*, 1895, **57**, 404). But he also contributed papers to the Society's *Journal* on water analysis and on lead salts, and to other journals on mineral oil and certain fatty oils. He was responsible for the article on "Explosives" in the first edition of Thorpe's "Dictionary of Applied Chemistry" and received a medal for a lecture on the same subject before the Royal Society of Arts.

Deering's knowledge of chemical literature was encyclopædic. He remained a student throughout his career and had an exceptionally retentive memory. There were few subjects upon which he could not, without hesitation, refer an inquirer to the more important papers dealing with them. In the laboratory, his work was characterised by meticulous care. He took nothing for granted, satisfied himself at every stage of the accuracy of his work, and eliminated or evaluated every possible source of error. He was a good linguist, speaking French and German fluently. He had also a working knowledge of Italian and the Scandinavian languages.

Inclined to be somewhat impulsive and outspoken, and intensely disliking insincerity of any kind, it was only those who knew Deering well who could realise his kindness of heart. He was incapable of an ungenerous act, and appreciated the work of his humblest assistant.

Deering lived for his work, and the Companionship of the Imperial Service Order, conferred upon him in 1906, was an inadequate recognition of a life of really devoted service to his country.

Deering married, in 1905, Isabel, daughter of Thomas Cowie of Blackheath. Upon his retirement, he moved to Devonshire and, after some years of failing health, died at Torquay on September 5th, 1925.

A. V. E.

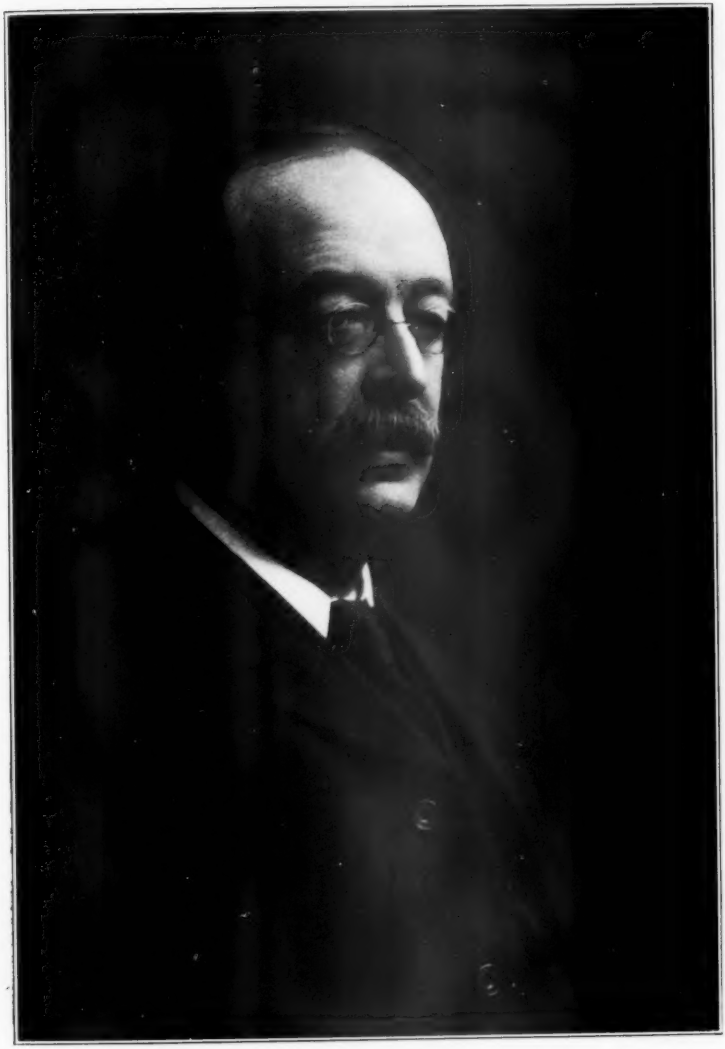
FRANCIS ROBERT JAPP.

BORN FEBRUARY 8TH, 1848: DIED AUGUST 1ST, 1925.

FRANCIS ROBERT JAPP, a member of a family of Dutch origin, whose name was well-known half a century ago in the eastern districts of Forfarshire, was born in Dundee on 8th February, 1848, the youngest son of James Japp, minister of the Catholic Apostolic Church in that city. His earliest education was obtained in the town of his birth, in part at the High School there; but in 1861, at the age of thirteen, he was sent to St. Andrews, the reputation of which as an educational centre stood then, as now, very high. After three years spent at the Madras College, he entered the University as a student in the Faculty of Arts.

The course of study for the Arts degree extended, at that time, over four winter sessions of five to six months each (there were no summer sessions), and the subjects studied were Latin, Greek, Mathematics, English, Logic and Metaphysics, Moral Philosophy, and Natural Philosophy. While at St. Andrews, Japp contracted a lifelong friendship with John Masson, essayist and author of "Lucretius, Epicurean and Poet."

After graduating M.A. at St. Andrews, Japp entered the University of Edinburgh in 1868 as a student of law; but his period of study at Edinburgh proved to be a short one. In the summer of 1869 his health broke down and he was compelled to relinquish his legal studies and to reside abroad, at Pau and at other health resorts. For two years, from the spring of 1871 to the spring of 1873, Japp resided in Germany, at Göttingen, Berlin, and Heidelberg; and although, during a portion of that time, he attended lectures on International Law and on German Literature, he had, even then, abandoned his intention of prosecuting the study of law. The record of the following two years will be more interesting if told in Japp's own words, communicated to the writer in a letter some years ago: "In the spring of 1873, I returned to England and spent the time partly in London, partly in Scotland. I had by this time taken up the subject of chemistry, in which I had always been interested. In the autumn of 1873 I returned to Heidelberg and began the study of that subject under Bunsen. I was then twenty-five years of age, and my friends, who had long despaired of my ever taking up anything seriously, regarded this last step as the crowning folly of a hopeless career. In 1875 I graduated Ph.D. at Heidelberg (only *insigni cum laude*). I was anxious to get all examinations behind me as soon as possible and, I fear, rather hurried matters. The Heidelberg Ph.D. at that time required no 'dissertation' and was rather a worthless degree;



Yours sincerely,
F. R. Jaffe.

[*To face p.* 1008.]

there was no practical examination—merely an ' oral ' of two hours. I stayed with Bunsen until the end of the summer semester, 1876, devoting the winter semester to the separation and preparation of various rare elements and the summer to a rather impossible piece of research which Bunsen had suggested and which led to no result. I also heard lectures by Hermann Kopp, on the History of Chemistry; by Hermann Quincke, on Physics; and by Blum, on Mineralogy. Contemporaries of mine in Bunsen's laboratory were John Gibson, J. E. L. Shadwell, C. Loring Jackson, W. F. Hillebrand, T. H. Norton, F. P. Treadwell, Charles Otto Trechmann, Hans Jahn, and Siegmund Gabriel."

From Heidelberg Japp proceeded to Bonn to work in the laboratory of August Kekulé, who had, some years previously, been appointed to the Chair of Chemistry in the University and had attracted to his Institute large numbers of young chemists of different nationalities. Whether the young Scottish chemist felt, as did van 't Hoff, that the laboratory of Kekulé was a sacred temple to be entered only with feelings of reverence and of awe, we cannot say; but the Memorial Lecture on Kekulé, delivered by Japp in 1897, bears, in its every line, clear and eloquent testimony of the esteem and admiration which he felt for his new teacher, who, although no longer at the height of his physical power, preserved his mental faculties unimpaired and could still inspire work of unsurpassed excellence. It was in the palatial laboratory at Bonn that Japp, under the more immediate guidance of G. Schultz and of Anschütz, first entered on that course of chemical investigation which he pursued with such wholehearted devotion and success for over thirty years. Among Japp's contemporaries at Bonn were P. Phillips Bedson, Henry Forster Morley, Richard Taylor Plimpton, and Shadwell.*

* The writer is indebted to Geheimrat Professor R. Anschütz for the following reminiscences of Japp's period of study in Bonn :

" Japp wohnte in Bonn mit seiner Mutter in einem Haus in der Kölnstrasse im Nordosten Bonns weit weg von dem in Poppelsdorf gelegenen chemischen Institut. Das beschränkte stark seinen Verkehr mit seinen Studiengenossen, die er nur im Laboratorium sprach; von studentischen Kneipereien hielt er sich fern. . . .

" Damals war Gustav Schultz Kekulé's Privatassistent und ich Vorlesungsassistent. . . . Soweit es meine Arbeiten für Kekulé gestatteten, arbeitete ich mit Schultz über das Phenanthren. Japp schloss sich an uns an und wir lernten im persönlichen Umgang die liebenswürdigen Eigenschaften des um einige Jahre älteren Fachgenossen schätzen, der nicht nur die deutsche Sprache völlig beherrschte, sondern sogar einen ausgesprochenen Sinn für den deutschen Volkshumor an den Tag legte. . . .

" Da Gustav Schultz und ich unsere Arbeitsplätze neben Kekulé im Privatlaboratorium hatten, so brachte es Japp's Entschluss mit uns zu

In 1878, Japp returned to Scotland and continued his research work in the laboratory of Professor Crum Brown, Edinburgh. Later in the same year he was chosen by Professor (later Sir) Edward Frankland, out of a large number of candidates, to take charge of the Research Laboratory which was then being established at the Normal School of Science, South Kensington, and to devote his whole time to the supervision of the research students. In 1881, when the Science Schools were reorganised by the Science and Art Department, Japp was promoted to the rank of Assistant-Professor in what was then called the Royal School of Mines and Normal School of Science, and which, at a later date, became the Royal College of Science. Here, under E. Frankland and later under T. E. Thorpe, who succeeded to the Chair of Chemistry in 1885, Japp continued to direct the work of research in, as well as to lecture on, organic chemistry. Although recognised as a brilliant research chemist, Japp felt that he was adversely affected in his candidatures for a Chair by his lack of experience in the conduct of a general laboratory, and in 1889, on the departure of P. F. Frankland to occupy the Chair of Chemistry at Dundee, Japp requested and was given a share in the teaching work of the large laboratories. Unsuccessful in his candidature for the Chairs at Leeds in 1885 and at Dundee in 1889, Japp was appointed to the Chair at Aberdeen in 1890, in succession to Thomas Carnelley.

The twelve years spent in London constituted, perhaps, the "Golden Age" of Japp's scientific life. Filled with an enthusiasm for research, Japp not only found his work at the Normal School (and Royal College) of Science for the most part congenial and satisfying, but he also greatly enjoyed participating in the active scientific life which found its focus in the Chemical Society, at the meetings of which he was often a conspicuous figure. In the discussions which there took place, as the writer is informed, "opportunity arose for his revealing, not only his dry humour, but also his profound knowledge of chemical literature and a width of classical and philosophical reading altogether beyond the range of the attainments of the great majority of his contemporary

arbeiten mit sich, dass er mit Kekulé genauer bekannt wurde, als es sonst geschehen wäre. Kekulé fand bald Gefallen an Japp's immer bedächtiger aber stets klarer Art sich in der Unterhaltung über wissenschaftliche Fragen auszusprechen.

"Als im Jahre 1878 die Stelle eines Demonstrator der organischen Chemie am Royal College in London bei Frankland zu besetzen war, bewarb sich Japp darum, unterstützt durch ein ausgezeichnetes Zeugnis von Kekulé, und Frankland gab ihm vor anderen Mitbewerbern den Vorzug. Wie mir Japp später mitteilte, habe Frankland besonders unsere Beweisführung der Konstitution des Phenanthrens gefallen."

chemical colleagues." Japp valued also the personal contacts with the leaders and fellow-workers in chemical science which residence in London made possible. On the other hand, Japp's scientific accomplishments, his well-stored and cultured mind, and his remarkable personality won the admiration, regard, and esteem of his fellow-chemists, and he was early called to serve on the Council and the Publication Committee of the Chemical Society. Although, to the great regret of his many scientific friends, Japp seldom, after his departure in 1890, re-visited London or took part in the gatherings of chemists elsewhere, one could not fail to note how, in later years when settled at the northern University, he sometimes looked back with something of wistful yearning to the inspiration and stimulating fulness of life which the Metropolis offered to the scientific worker.

While at the Royal College of Science, Japp gathered round him a large number of able and enthusiastic students, and research was prosecuted with great activity. About half the total number of scientific papers which Japp published, either independently or in collaboration, appeared during his London period.

During this period, also, Japp contributed to the advancement of chemistry by the publication, in collaboration with E. Frankland, of a text-book of Inorganic Chemistry which was "constructed on those principles of Classification, Nomenclature, and Notation which, after an experience of nearly twenty years, have been found to lead most readily to the acquisition of a sound and accurate knowledge of elementary chemistry." The composition of the book was mainly the work of Japp, and the more theoretical sections, such as the chapter on the Atomic Theory, are excellent examples of clear and well-reasoned exposition. Owing, doubtless, to the adoption of Frankland's constitutional formulæ and nomenclature, which did not find favour with contemporary chemists, this work did not have the circulation which it deserved.

Japp also collaborated with Frankland in the preparation of a new edition of the latter's "Lecture Notes on Organic Chemistry."

From the Royal College of Science Japp proceeded, as has been noted, to the University of Aberdeen. He was, perhaps, fortunate in the date of his appointment, for it fell on the eve of a very great and rapid development of the University, marked, not only by the erection of imposing buildings and an increase in the number of its teachers, but also by a renewed activity in literary and scientific investigation. In all this progressive movement the Chemistry Department, under Japp's guidance and enthusiasm, played a notable part.

Until 1896, the Chemistry Department of the University of

Aberdeen was housed in a series of four or five small rooms, badly lit and badly ventilated, which afforded accommodation of a very inadequate character for only two or three advanced students working at one time. Two of the rooms, in which the classes in practical chemistry for medical students were held, were fitted with a circular table without sink and without water-supply other than that contained in a jug placed on the narrow working bench. In these rooms even the most primitive arrangements for the extraction of fumes were wanting, so that when fifteen or twenty students were vigorously boiling off excess of aqua regia, the figure of Japp, seated on a stool in the centre of the space enclosed by the circular work-bench, could be only faintly discerned through a mist of acid vapours.

With such accommodation at his disposal, it was clear that it would be impossible to build up a school of chemistry of any importance, and Japp therefore set about the task of arousing public opinion and of stimulating the University authorities to a recognition of the claims of chemistry to more adequate accommodation. His reward came at last, and in 1896, with the carrying out of a scheme of University extension, Japp found himself installed in laboratories which, at that time, could be regarded as palatial, but which, in the space of thirty years, have become inadequate for the requirements of the present day.

Development, however, took place in directions other and more important than towards new buildings. Previously, the work of the Chemistry Department had consisted, almost entirely, in the teaching of elementary chemistry to medical students, but soon after Japp's installation as Professor at Aberdeen, a Faculty of Science was instituted, courses of instruction leading to the degree of B.Sc. were introduced, and a school of advanced chemical study rapidly grew up. It must, indeed, be regarded as not the least important and valuable of Japp's contributions to the advancement of chemical science that, in an area where there had previously existed no school of advanced chemical training or tradition of chemical study, he created a vigorous school of chemical instruction and research from which there has issued a succession of chemists, many of whom occupy important academical and industrial posts in various parts of the world.

While at Aberdeen, Japp delivered, each year, two courses of lectures, one on elementary inorganic chemistry and one on organic chemistry; and it must be confessed that as a lecturer to young Scottish students, perhaps the most testing audience for any lecturer to address, Japp fell somewhat short of achieving complete success. It may be that he did not sufficiently bear in mind that

the great majority of the students attending his elementary class came to him entirely ignorant of chemistry or were hearing his lectures, not from choice, but under the compulsion of regulations; and it may also be that he was, temperamentally, somewhat out of touch with the mind of the average young student. As a consequence, the generous appreciation of which the Scottish student is capable sometimes degenerated, unfortunately, into an irritating disturbance or even a boorish noisiness. This behaviour on the part of his students was a constant source of annoyance and worry to Japp, and even told adversely on his health. On one occasion, when the disturbance was more than usually bad, Japp was roused to protest. Halting in the course of his lecture, he gazed on his students for a few moments and said: "Gentlemen, I have been a member of four Universities—London, Edinburgh, St. Andrews, and Aberdeen—and I find that the higher the latitude the lower the breeding."

For his comparative lack of success with his elementary class, his success as a lecturer on organic chemistry to advanced students in science must have been some compensation. In this case, the lecturer was dealing with a branch of chemistry to which he had devoted his life and he was in the presence of a serious body of students to whom he gave of his best. Drawing on his wonderful knowledge of the subject and brightening, here and there, the intricacies of a problem in constitution with a touch of personal reminiscence, Japp revealed to his students the main features and course of development of organic chemistry in a manner which, to the student, was most impressive and showed Japp's mastery of detail, clearness of thought, and accuracy of language.

In all his teaching, whether in the lecture room or in the laboratory, Japp was intolerant of haziness of thought and slovenliness of manipulation; and the high standard of clear thinking, accurate expression, and neatness of experimental work which he set for himself and demanded of his students did not fail to make an ineffaceable impression on his pupils.

It was, however, in the research laboratory that Japp was most at home and at his best. With the help of a research assistant, maintained by means of a grant from the Royal Society, and in later years with the assistance of his own graduate pupils, Japp was enabled to maintain, although in somewhat diminished volume, his output of research work. During his tenure of the Chair at Aberdeen, upwards of forty papers were published by Japp in collaboration with his private assistants or research students. Although the last paper to bear his name appeared in 1905, Japp continued to inspire and direct the research work of members of

his staff; and, with a modesty approaching almost to self-depreciation, he frequently effaced himself in order that his reputation and seniority might not deprive his younger colleagues of any credit to which they might be entitled. This self-effacement was exhibited, not only in connexion with the publication of research, but also in connexion with the organisation and development of the teaching work of his Department.

Although always jealous of the interests of his Department and active in its development, Japp took no prominent part in University politics or in the general work of administration. Nor did he take much part in the life of the various University Societies. "Whenever they" (the officials of the societies) "came to me for an address, I used to give them a sovereign, which I have no doubt was infinitely more acceptable." This, of course, was not the case, and one cannot but regret, from the point of view of the students, that Japp refrained from making use of the opportunities which offered of impressing on a larger body of the students something of his own remarkable personality, of imparting to them something from his great store of scientific and literary lore, and of encouraging in them the cultivation of the wide and philosophic outlook which he himself possessed. Japp, however, had little of the missionary spirit and no great love for the platform or the market place; and he preferred to share the treasures of his mind chiefly with those who were associated with him in research or had the good fortune to enjoy his friendship.

Commencing, as Japp did, his career as a chemical investigator in the laboratory of Kekulé, who, to quote from the Memorial Lecture, "brought an intellect of incomparable power and subtlety to bear on problems so abstruse, so remote from the everyday thoughts and interests of mankind, that the vast majority even of educated persons have never heard either of the problems or of the man who did so much to solve them," it is, perhaps, not surprising that Japp's research work was by no means "popular." It concerned itself at no point with problems of everyday experience or of immediate industrial importance, but dealt with many difficult problems of chemical constitution which required for their solution greater chemical acumen and a more profound knowledge than is the case with many investigations which make a more direct appeal to the lay mind. Endowed with a very retentive memory, Japp took to heart, and passed on to his pupils, the counsel which Liebig gave to Kekulé: "If you want to be a chemist, you will have to ruin your health; no one who does not ruin his health with study will ever do anything in chemistry nowadays." The *Journal of the Chemical Society*, the *Berichte*, and

the *Annalen* were Japp's constant companions, and the *Jahresbericht* formed his holiday reading. As a result he acquired an incomparable knowledge of organic chemistry which, together with a great capacity for accurate and laborious experimental work, the power of clear thinking and reasoning, and a highly developed "chemical instinct," enabled him to solve successfully many obscure problems of chemical constitution. Japp, moreover, was imbued with the spirit of the true scientific investigator intent only on eliciting the truth, without thought of personal ambition or material gain.

The raw materials of almost all of Japp's research work were phenanthraquinone, benzil, and benzoin; and from a paper (J., 1897, **71**, 123) which may almost be regarded as the *apologia* of his scientific life one learns that the main objects of the systematic study of the condensations of the ketones and keto-alcohol mentioned were the synthesis of cycloids and the comparison of the properties of ortho-diketones of the aromatic series with those of the α-diketones or keto-alcohols of the aliphatic series. As he pointed out: "At that time, Ladenburg's 'prism' formula could still be seriously put forward as a satisfactory expression of the reactions of benzene; and in this formula the ortho-carbon atoms are not directly united. Every condensation, therefore, which bore out the foregoing analogy" (between aromatic and aliphatic α-diketones) "was a fresh argument against the 'prism' formula. Indeed, it is cumulative evidence of this character, rather than any definite disproof, that has caused the 'prism' formula to be withdrawn from discussion."

It may be remarked that some of Japp's earlier investigations (*e.g.*, J., 1880, **37**, 410; 1882, **41**, 146), which were undertaken partly with the object of throwing light on the constitution of phenanthraquinone itself, supported Graebe's peroxide formula; later work, however (*e.g.*, J., 1883, **43**, 27), furnished a very strong argument in favour of Fittig's formula, which was subsequently always employed.

The success with which the main object of Japp's research work, the synthesis of cycloids, was realised, is well seen from the following list of the various classes of compounds formed in different condensation processes:

Oxazoles.—1. By the interaction of α-diketones with aldehydes and ammonia (J., 1880, **37**, 669; 1881, **39**, 225). 2. From benzoin and nitriles (*ibid.*, 1893, **63**, 469).

Iminazoles.—1. *Ordinary* (*secondary*) *Iminazoles.*—From α-diketones, aldehydes, and ammonia (*ibid.*, 1882, **41**, 146, 157, 323; 1886, **49**, 464; 1887, **51**, 552, 557). 2. *Tertiary Iminazoles and*

Quaternary Ammonium Compounds. From α-diketones and primary amines of the formula $R{\cdot}CH_2{\cdot}NH_2$ (*ibid.*, 1895, **67**, 32).

Furfurans.—By the action of hydriodic acid on the condensation products of α-diketones with ketones (*ibid.*, 1890, **57**, 662).

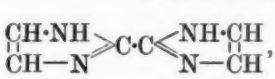
Indoles.—By the condensation of benzoin with primary benzenoid amines (*ibid.*, 1894, **65**, 889).

Azines.—By the action of ammonia (1) on benzoin and (2) on α-diketones (*ibid.*, 1886, **49**, 828; 1887, **51**, 98).

To the above series of compounds one may also add *lactones*, *pyrrolones*, and *pyrroles*.

In addition to the foregoing classes of compounds, all of which are heterocyclic, a number of pentacarbon ring compounds were also synthesised. Chief among these are *anhydracetonebenzil*, obtained by the condensation of benzil with acetone (J., 1885, **47**, 21); *anhydracetonebenzilcarboxylic acid*, by the condensation of benzil with acetonedicarboxylic acid (J., 1897, **71**, 139); and two isomeric *anhydrobenzil-lævulic acids*, by the condensation of benzil with lævulic acid (J., 1897, **71**, 144).

For the most part, the superstructure of Japp's synthetic work was founded on a new reaction which he discovered, the condensation of ketones with aldehydes in presence of ammonia, and on his use of caustic potash as a condensing agent. The careful investigation of a large number of such condensation reactions and the elucidation of the constitution of the compounds produced in these reactions or prepared as derivatives therefrom, not only formed a very important and valuable contribution to synthetic organic chemistry, but also enabled Japp to elucidate the constitution of important compounds prepared by other investigators. Thus, by condensing benzil with benzaldehyde in presence of ammonia, lophine was obtained, and the constitution of this compound, first prepared by Laurent and by Fownes, was thus shown to be $\begin{matrix} C_6H_5{\cdot}C{\cdot}NH \\ \| \quad\quad > \\ C_6H_5{\cdot}C{-}N \end{matrix}$$>C{\cdot}C_6H_5$. By the reduction of lophine, amarine, $\begin{matrix} C_6H_5{\cdot}C{\cdot}NH \\ \| \quad\quad > \\ C_6H_5{\cdot}C{\cdot}NH \end{matrix}$$>CH{\cdot}C_6H_5$, is formed (J., 1882, **41**, 323; 1900, **77**, 608). Further, condensation of benzoin with benzonitrile under the influence of concentrated sulphuric acid showed that Laurent's benzilam (Zinin's azobenzil) is triphenyloxazole; and the oxidation of anhydracetonebenzil to desyleneacetic acid and the reduction of this acid to βγ-diphenylbutyric acid, which was found to be identical with Zinin's pyroamaric acid, established the constitution of the latter. By other condensations, also, important light was thrown on the constitution of glyoxaline, $\begin{matrix} CH{\cdot}NH \\ \| \quad\quad > \\ CH{-}N \end{matrix}$$>CH$,

glycosine,  , and lepiden (tetraphenyl-furfuran).

Whilst the scientific investigations to which reference has just been made established Japp's reputation as a chemist of the first rank, the address which he delivered as President of the Chemistry Section of the British Association in 1898 made a wider appeal, and showed that he was not a mere specialist with his interests confined within the bounds of his own narrow branch of work, but that he interested himself also in the more fundamental problems of science and of life.

In that address, Japp emphasised the importance of the discoveries in stereochemistry because they furnish a reply "to the most fundamental question that physiology can propose to itself—namely, whether the phenomena of life are wholly explicable in terms of chemistry and physics; . . . or whether, on the contrary, there are certain residual phenomena, inexplicable by such means, pointing to the existence of a directive force which enters upon the scene with life itself, and which, whilst in no way violating the laws of the kinetics of atoms, determines the course of their operation within the living organism." His whole address was an argument, based on the results of stereochemical investigation, in favour of the doctrine of vitalism as revived by the younger physiologists; and in it his purpose was to show that "living matter is constantly performing a certain geometrical feat which dead matter, unless, indeed, it happens to belong to a particular class of products of the living organism and to be thus ultimately referable to living matter, is incapable—not even conceivably capable—of performing."

The argument may be briefly summarised. Although in nature most asymmetric compounds occur in one of the optically active forms only, it is found that when it is attempted to synthesise such a compound from symmetric substances the product of the synthesis is always inactive. As Pasteur said: "Artificial products have no molecular asymmetry; and I could not point out the existence of any more profound distinction between the products formed under the influence of life and all others." The inactive forms, however, obtained by chemical synthesis can be resolved into the two oppositely active isomerides by means of enzymes, moulds, etc., and even, in some cases, by crystallisation. Since the racemic sodium ammonium tartrate could be resolved into the active forms by the symmetrically acting process of crystallisation, and these active forms could be separated by hand, it was thought that "the barrier which M. Pasteur had placed between natural

and artificial products" was thereby broken down; and this was undoubtedly the view held by the majority of chemists.

But had it? Japp intimated in his address that he had for some time held a contrary opinion, and he again asked the question which had also previously been posed by Crum Brown: "Is not the observation and deliberate choice by which a human being picks out the two kinds of crystals and places each in a vessel by itself the specific act of a living organism of a kind not altogether dissimilar to the selection made by *Penicillium glaucum?*" This question Japp discussed and answered in the affirmative. The artificial, racemic compound, certainly, had been resolved into the active forms by the symmetrical process of crystallisation, but these two forms had not thereby been *separated* from each other; both active forms were present side by side. Their separation "requires the living operator, whose intellect embraces the conception of opposite forms of symmetry, to separate them." . . . "Conscious selection here produces the same result as the unconscious selection exercised by the micro-organism, the enzyme, or the previously existing asymmetric compound." Pasteur had himself pointed out that "to transform one inactive compound into another inactive compound which has the power of resolving itself simultaneously into a right-handed compound and its opposite, is in no way comparable with the possibility of transforming an inactive compound into a *single active* compound. This is what no one has ever done; it is, on the other hand, what living nature is doing unceasingly before our eyes." Here then is the conclusion to which, from a consideration of the facts of stereochemistry, Japp arrived: "The production of single asymmetric compounds, or their isolation from the mixture of their enantiomorphs, is the prerogative of life. Only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can produce this result." And further: "I see no escape from the conclusion that, at the moment when life first arose, a directive force came into play—a force of precisely the same character as that which enables the intelligent operator, by the exercise of his will, to select one crystallised enantiomorph and reject its asymmetric opposite." The action of such a directive force, moreover, involves no violation of the law of the conservation of energy.

An address on such a subject as that selected by Japp could not fail to provoke discussion, and its arguments were, indeed, assailed by Karl Pearson, Fitzgerald, Herbert Spencer, and others. All their criticism, however, was successfully met, and failed to force a retreat from any of the positions which had been taken up.

That the work which Japp accomplished for chemistry was appreciated by the scientific and academic world is shown by the honours of which he was made the recipient. As early as 1885, he was elected a Fellow of the Royal Society; from 1885 to 1891, he was Foreign Secretary, and from 1895 to 1899, Vice-President of the Chemical Society; in 1891, he was awarded the Longstaff Medal, the highest mark of appreciation which British chemists can show, for his researches in organic chemistry; in 1898, he was President of the Chemistry Section of the British Association; and from 1901 to 1904, he was Vice-President of the Institute of Chemistry. In 1888, the University of St. Andrews conferred on Japp the Honorary Degree of LL.D., and he was similarly laureated by the University of Aberdeen in 1915.

A sketch of Japp's scientific achievements, however, gives a picture of but half the man; for in him we find one who, although a specialist who won for himself high distinction in a relatively narrow field of scientific study, nevertheless appreciated and loved literature and art. A linguist of ability, the literatures of England, Germany, France, and Italy were accessible to him in the language of their authors; and while possessing a familiar knowledge of all that is best in the literature of our own country, his acquaintance with the literature of Germany, of France, and of Italy was such as might be envied by many who have taken up the study, not of science, but of letters. On many occasions an apt quotation or literary allusion gave point to an argument or brightened a conversation.

In his speech, as in his writing, Japp's language was always clear and accurate, and if he did not compose with rapidity he did so with exceeding care; and his writings were models of lucidity, logical development of an argument, and accuracy of expression.

Japp's interests extended, also, into the realm of Art, especially of music. A musician of cultivated taste, he possessed not only executive ability as a pianist but also a thorough knowledge of musical theory and a wide acquaintance with musical compositions. It was to him a great pleasure, relaxation, and recreation to spend an evening, in the company of music-loving friends, in discussing the compositions of his favourite composers or in performing their works.

Unskilled in the art of self-advertisement and indifferent to the world's estimates of eminence or wisdom, Japp looked upon the general activities of the world and the impatient hurrying of men with a certain Olympian detachment and philosophic calm; and the petty annoyances which were laid upon him by the jealousies or inconsiderateness of lesser minds he bore with amiable

resignation. He was slow to form conclusions, but his judgment, whether of men or of opinions, was sound and could be relied on with confidence. He was himself the soul of honour and devoted to truth.

A product of the old *régime* in Arts in the Scottish Universities which, whatever its defects, cultivated width of view and diversity of outlook, Japp looked out on life through many windows, and to know him was in itself a liberal education.

In 1914, Japp retired from the Chair of Chemistry at Aberdeen and resided at first at Acton and later at Richmond, where he died. The closing years of his life were saddened by the loss of his son, who died, in 1920, while on the threshold of a promising career, from an illness contracted while on military service. In 1921, Japp's health broke down and he had to undergo an operation from which he never fully recovered; and in his last years, failure of eyesight deprived him of the companionship of books.

In 1879, Japp was married to Elizabeth Tegetmeyer, of Kelbra-Kyffhäuser, a small town near Nordhausen, by whom together with two daughters he is survived. A. F.

FRANCIS JONES.

BORN 1845; DIED OCTOBER 22ND, 1925.

FRANCIS JONES was born in Edinburgh in 1845 and was educated at the Edinburgh Institute and the University. He went to Heidelberg to work under Bunsen, and here he met Roscoe. On returning to England he became one of Roscoe's two assistants in the great work on the atomic weight of vanadium. For Roscoe he always expressed great admiration, but it was a disappointment to him that no acknowledgment of his help appeared in the great paper. He used to say, with a whimsical smile: "I was only referred to as Analyst A or Analyst B, I forget which." On the retirement of Dr. Marshall Watts, Jones was appointed chemistry master at the Manchester Grammar School. The High Master was then F. W. Walker, one of the few non-clerical headmasters at the time. Realising, as few of his confrères did, the possibilities of science as a means of education, he gave Jones a free hand, and success came at once. Scholarships at the older universities were offered for science, and Manchester secured a very large number. In 1879, no fewer than thirteen of these coveted distinctions were won by Manchester boys, probably a record for the science side of any school. There was no extra preparation for scholarship boys, either in physics or in chemistry. Both Jones and

John Angel, the physics master, believed in letting boys teach themselves and each other, and, beyond the formal lectures and a little instruction in the chemical laboratory, the masters left the boys to work out their own salvation. To a modern schoolmaster, the liberty allowed to the Science Sixth would seem incredible. Many an afternoon would be spent in the Manchester Free Library, or in the ever-delightful quietude of the fifteenth-century library of the Chetham Hospital near by.

Besides Jones's personality, what affected us boys most was seeing him always at work on research. Many of those who have since given their lives to original investigation, owe most of the impetus which has driven them on, to the work on boron hydride which they watched in progress. The complete destruction of a large charcoal stove in which boron trioxide was being heated with magnesium, and the carrying off of R. L. Taylor, Jones's collaborator, to the infirmary, were incidents which made an impression never to be effaced on those of us who saw it.

In the new laboratory at the top of the main block of buildings, Jones had at last a place worthy of himself. His special pride was a very large and well-ventilated draught cupboard. In this the writer attempted, in its first week, the isolation of the still unknown oxide of bromine. About 15 c.c. of liquid monoxide of chlorine were mixed with a quantity of dried silver bromide, and not only was all the frame work and glass shattered to pieces, but the 3-inch slate bed was broken. All Jones said, when he contemplated the wreckage, was : " Well, it was what it was made for."

He died, at the age of 80, on October 22nd, 1925. His memory will always be cherished by his old pupils, who were also his friends. No schoolmaster had an influence like his on the making of a chemist.

H. B. B.

EDMUND KNECHT.

BORN JANUARY 29TH, 1861; DIED DECEMBER 8TH, 1925.

EDMUND KNECHT was born in Liverpool. His father, Gustav Knecht, B.Sc. (London), was a man of exceptional gifts as a schoolmaster, and his mother a Lancashire woman of singular charm. When Edmund was ten years old, the family settled in Southport, where his father conducted a school with much success for several years. From here the family, consisting now of three daughters and two sons, moved to the neighbourhood of Zurich, where a residential school was started on a largish estate. But the responsibilities and worries attendant thereon were too heavy and the

Knechts finally moved into Zurich itself. Edmund by this time was of an age to enter the University. He had natural leanings towards engineering, in fact his manipulative and mechanical skill was very marked. It was, however, his quick perception and interest in chemistry which attracted the notice of Victor Meyer, then Professor at Zurich University, and he induced Knecht to take up the study of this branch of science. At the age of twenty-one Knecht secured his Ph.D., his thesis being concerned with the homologues of resorcinol, and ultimately he became assistant to Victor Meyer. At this time Knecht saw a good deal of Sandmeyer, and the two remained all their lives the closest of friends.

Knecht soon after (1883) was offered the post of Head of the Chemistry and Dyeing Department of the Bradford Technical School which he occupied until, in 1890, there came a call to the Manchester College of Technology, in which institution he was actively engaged for the remainder of his life, as Professor of Tinctorial and Technological Chemistry, or as Associate Professor of Applied Chemistry of the University of Manchester. During a considerable portion of these thirty-five years Knecht was hard at work most days, including three evenings a week as well as Saturday afternoons. His influence on the students was remarkable both in the laboratories and in the lecture room. Few men of his time had so great a gift of inspiring their students with enthusiasm for their subject. Not only at home, but throughout the world, there must be thousands who have had the benefit of his tuition and his influence, and who regarded him with the utmost esteem both as a teacher and for his genial human qualities. His interest in his students did not stop with the conclusion of their academic career. He was wonderfully successful in finding them suitable posts, keeping track of them afterwards, and maintaining an interest in their future. Many are the chemists who would not hesitate to ascribe largely to Knecht's influence whatever success they have attained.

When the Society of Dyers and Colourists was formed in 1884, Knecht was appointed Editor of the Journal (1884—1893), which position he afterwards shared first with C. Rawson (1893—1899) and later with Professor W. M. Gardner (1899—1925). A large number of members assembled last year to commemorate the fortieth year of Professor Knecht's editorship and to make a handsome presentation to him subscribed to by his admirers, resident in all parts of the world.

The editing of the monthly journal just referred to claimed Knecht's close attention, but despite this he published in 1889 in conjunction with Benedict, "Chemistry of Coal Tar Colours," then

in conjunction with Christopher Rawson and Dr. R. Lowenthal that very widely-known text-book, "A Manual of Dyeing," unique of its kind; another treatise, "The Principles and Practice of Textile Printing," was published in conjunction with J. B. Fothergill. Yet another publication is entitled, "New Reduction Methods in Volumetric Analysis," by himself and Eva Hibbert. Many of the new analytical methods described in this volume have been widely adopted in chemical works at home and abroad. The methods are specially applicable to the rapid volumetric estimation of a great variety of substances including iron, sugar, and many dyestuffs. Two editions of all these books have been printed. Knecht was a contributor of many articles to the "Encyclopædia Britannica" as well as to Thorpe's "Dictionary of Chemistry."

Knecht's original research work is recorded in some 120 papers in the *Journals* of the Society of Dyers and Colourists, the Chemical Society, and the Society of Chemical Industry, the *Berichte*, and elsewhere. An enumeration of the titles of all of them appeared in the first-mentioned journal in June, 1925, and February, 1926. His contributions to our knowledge of chemistry range over an extraordinarily wide field. Many are closely connected with industrial, others again with pure chemistry. The major part of his researches was in relation to the chemistry of dyes, to the theory of dyeing, and to the application and manufacture of dyes. But as a glance at the titles of his many papers will show, he gave particularly close attention to all matters connected with the chemical and physical properties of textile fibres, especially cellulose and its derivatives, and he published interesting researches on the constitution of soot, and French and American rosin.

Knecht's system of volumetric analysis by the use of titanous salts, originally only intended to be applicable to the estimation of organic dyestuffs, has been so widely extended as to cover analysis of a great variety of other organic, as well as inorganic, substances. The extraordinarily wide applicability of these methods of volumetric analysis are regarded by some as being of such great importance as even to overshadow his brilliant work on dyeing and the chemistry of cellulose.

Knecht's memory was prodigious and, having read widely, he kept himself well up to date in all that touched upon the chemistry of dyes and of dyeing and of textiles. In these domains he was a perfect walking encyclopædia and could refer one, with unfailing trustworthiness, to almost any source of information upon which one desired enlightenment.

Knecht's modesty was characteristic of so many truly great men; his heart was absolutely in his work, with little or no thought of personal advancement or financial benefit to himself.

The circle of his friends and admirers was a very wide one, although he was not much given to indiscriminate social activities. Probably he felt these might interfere too much with his always strenuous work.

As years advanced, Knecht's zeal and enthusiasm for his research work seemed to grow keener and more intense. This was true up to within a few weeks of his death. He then underwent two serious operations. From the effects of these he had not quite recovered when in December, after two months spent in Switzerland, he returned home in very trying weather conditions, as a result of which he quickly succumbed to an attack of bronchitis and, his heart being unable to withstand the further strain, he breathed his last at Marple in the county of Cheshire, where he had made his home for so many years.

I can say without hesitation that I have rarely come across a man who so well deserved the esteem and affection and gratitude of a great body of chemists. A host of them owe to Edmund Knecht that sound basis of scientific thought and enthusiasm for their subject without which so little can be accomplished that is truly worth while in the domain of chemistry. He did his best in his own special sphere of activities and none will deny that his best was very good.

ALFRED RÉE.

WILLIAM ROBERT LANG.

BORN 1870; DIED NOVEMBER 20TH, 1925.

THE late William Robert Lang was a graduate of the University of Glasgow (B.Sc. 1890, D.Sc. 1899) and resigned the lectureship in Organic Chemistry there to become Professor of Chemistry in the University of Toronto. He was a Fellow of the Chemical Society (1897) and a member of the Institute of Chemistry and was elected Fellow of the Royal Society of Canada in 1911.

One of Dr. Lang's first activities in Canada was the promotion of a Canadian Section of the Society of Chemical Industry, of which he was the first Chairman. His scientific interests lay chiefly in the application of chemistry to industrial problems, and his monograph on the chemical industries of the Dominion (*Trans. Can. Inst.*, 1905) formed the basis of the "Directory" published by the Canadian Government in 1921. Many other papers in the chemical journals bear his name, or the names of his students.

From 1889 until the day of his death, Dr. Lang was actively connected with the forces of the King. In Glasgow, his birthplace (1870), he served with the Lanarkshire Royal Engineers (Volunteers); the year of his arrival in Canada he was gazetted to the Second Field Company Canadian Engineers, which he commanded as Major (1902) and Lieutenant-Colonel (1912); at the coronation of King George V in 1911 he commanded the Canadian Infantry there present. On the outbreak of war in 1914 he was appointed to the Canadian General Staff, assumed the duties of Officer in Charge of military instruction for Military District No. 2, and became O.C. the University of Toronto contingent of the C.O.T.C. In 1917 he was gazetted Colonel, and in the following year was G.S.O. (1) Coast Defence in the Maritime Provinces at Halifax N.S.

At the close of the war, Colonel Lang resumed command of the reorganized C.O.T.C. contingent, and resigned the professorship of Chemistry to direct the Department of Military Studies newly established in the University of Toronto; to the excellence of his work in this capacity high tribute was paid by Major-General MacBrien, Chief of Staff of the Canadian Militia, and a very keen critic, when at last year's inspection he said: "This is the largest O.T.C. inspection I have ever seen—and also the best."

Dr. Lang died very suddenly on November 20th last; the military funeral was preceded by a service at the University.

W. Lash Miller.

FRANK GEORGE POPE.

Born November 13th, 1867; Died October 29th, 1925.

Frank George Pope was born on November 13th, 1867, the son of George Campion Pope and Teresa Pope. He received his early education at Haberdashers' School and afterwards proceeded to Finsbury Technical College with the intention of becoming an engineer. This intention was not realised, as he went to the Peoples' Palace Technical Schools as a demonstrator in the Chemical Department. At that time, East London College had not been thought of, and it was necessary to deal, not with matriculated students working for a degree, but with boys of 12 to 15 years of age belonging to a large day school and to spend four nights a week on evening classes, principally attended by junior works chemists and elementary teachers. Luckily, no classes were held on Saturdays.

When I first met Pope one evening in February, 1894, he was running a practical class of the stamp usual in those days and

trying to do some research in the store-room, as he had no private bench of his own at which he could work. The next month we joined forces and started a firm friendship which only ceased with his lamented death last October. Had it not been for his help, kindness, and extreme loyalty, my earlier days at the People's Palace would have been very different. Pope could manage boys; not being used to them, I could not. His methods were summary but just, and many an old boy must remember the penalties exacted for not taking down notes properly during lecture. Whilst boys had to work hard and keep the peace when in class, once the week's work was done, Pope would play cricket with them on Saturdays and for years attended the annual camp of Day School boys on the South Coast.

Pope very soon joined in some work that was interesting me; this was kept going at odd times between classes and, on Saturdays, we often met about 2 p.m. and went on until 10. Our earliest joint publications were concerned with fluorones, the "abnormal hydrates" formed by hydroxyazo-compounds and one or two new hydrazines. The fluorones especially interested Pope and he returned to their study in later years, his work (partly with H. H. Howard) and that of Kehrmann clearing up many doubtful points.

In the later 'nineties, the nucleus of East London Technical College was formed with a number of day boys who had finished their three or four years' course and could be put on to more advanced work; in this way, a supply of research assistants was at last assured. Meanwhile, Principal Hatton was striving for the establishment of an East London College. Such a college has now been a school of the University of London for some years past.

A good knowledge of organic chemistry and great interest in the subject, together with a genial disposition, made Pope an excellent teacher. After an advanced organic lecture, he would come with the class into the laboratory, walk to a blackboard, start asking questions, expound views, and make the students show what they did or did not know.

From 1915, until the chair of chemistry was filled by the appointment of Professor Partington, Pope acted as head of the Chemical Department, and the College authorities made him an Assistant-Professor. He had been a Reader in the University for some years. The burden during the war was considerable and the subsequent work heavy, as East London College, like other institutions, suffered from a surfeit of students.

During a well-earned holiday in 1922, peritonitis supervened on food poisoning and after an operation in Switzerland it was some months before Pope returned to England. For a time, he con-

tinued his work at East London College, but it was evident that his health was broken and he had to retire in 1923. His old students and colleagues made him a presentation at the Old Students' Association dinner in January, 1925. This was the last College function he attended. After further months of illness, he died on October 29th, 1925.

Pope was beloved by his pupils and colleagues. Students who shirked or exhibited too much conceit had reason to regret their faults, but anyone who desired aid found in him a ready helper. Like many other chemists, he enjoyed out-door life and it was a delight to sit with him on a Surrey hill, not bothering about the time of lunch or the return train to London.

He married Adelaide, daughter of Harold Field Downer. She and a married daughter survive him to mourn his loss. His old students and former colleagues remember a very unselfish friend to whom they owed many a debt for uniform kindness and consideration. No one realises this more fully, or holds his memory in deeper affection, than the present writer.

J. T. HEWITT.

CHARLES ETTY POTTER.

BORN JANUARY 5TH, 1880: DIED SEPTEMBER 13TH, 1925.

CHARLES ETTY POTTER was born on January 5th, 1880, at Melsonby, near Darlington, at which place his father was headmaster of the Wesleyan school. An early aptitude for school work enabled him to gain a Flounder's scholarship with which he entered the North Eastern County School at Barnard Castle, and a successful school career was terminated by the winning of a North Riding scholarship tenable at the Yorkshire College. In his studies at Leeds, Potter's attention was directed to the physical sciences, and after graduating as B.Sc. of Victoria University in 1900, he pursued a post-graduate course in applied chemistry under Professor H. R. Procter in the leather industries department. In the development of various social activities at the Yorkshire College, Potter took a very active part, and the students' scientific, debating, and other societies were indebted in no small measure to his energy, enthusiasm, and determination.

On leaving the Yorkshire College in 1901, Potter accepted a post on the research staff of the Wellcome chemical research laboratories, where, for some years, in collaboration with Dr. F. B. Power and Dr. H. A. D. Jowett, he was engaged in the investigation of problems connected for the most part with complex organic compounds. Three papers published in the *Journal* of

the Chemical Society conjointly with H. A. D. Jowett, namely: "Preparation and Properties of 1 : 4(or 1 : 5)-Dimethylglyoxaline and 1 : 3-Dimethylpyrazole" (J., 1903, **83**, 464), "The Constitution of Chrysophanic Acid and of Emodin" (*ibid.*, p. 1327), "The Constitution of Barbaloin" (J., 1905, **87**, 878), indicate the nature of the work on which he was engaged. The *Pharmaceutical Journal* affords a record of other work with which Potter was associated during this period.

In January, 1906, Potter was transferred to a position in the analytical department at the Dartford works of Messrs. Burroughs Wellcome and Co., but towards the end of the same year he decided to take up teaching work. For a short time he was engaged at the Abergele Council school, but his chief teaching work was done at the Heckmondwike Secondary school where for 10 years he was engaged in teaching chemistry, physics, and mathematics and was responsible for the organisation of courses of instruction in physical science adapted to the requirements of a scheme of home training for girl pupils. For the greater part of this period he was also in charge of evening chemistry classes at the Batley Technical College. Early in 1916, he obtained an appointment as research chemist with Messrs. Levinstein, Ltd., at Blackley, Manchester, which position he retained after the amalgamation of Messrs. Levinstein with British Dyes, Ltd., and at the time of his death he was in the service of the British Dyestuffs Corporation, Ltd. As a member of the staff of the technical research department in this concern Potter was not only associated with the laboratory research work on colouring matters, but with problems incidental to large-scale production; he also held a position of considerable responsibility in connexion with the engagement and welfare of chemical assistants in the technical departments. He took a keen interest in the activities of the Manchester sections of the Society of Chemical Industry and the Institute of Chemistry, and served on the Committee of the latter for a period of three years.

Many of his Yorkshire friends had an opportunity of meeting him at the annual meeting of the Society of Chemical Industry at Leeds in July, 1925. Those who took part in the excursion to Huddersfield were particularly impressed by the lively and illuminating manner in which Potter explained certain of the processes carried on in the works of the British Dyestuffs Corporation. Towards the end of the same month he became seriously ill as the result of an insect bite on the scalp, and, in spite of every attention, died in the Manchester Royal Infirmary on the 13th September, and was buried in the grounds of St. Margaret's church at Prestwich on September 16th. He left a widow and three sons of school age.

For information relating to Potter in the period subsequent to his University studies, the writer is much indebted to Mr. F. H. Lees, the Head of the analytical department of Messrs. Burroughs Wellcome and Co. Potter is described by him as an enthusiastic worker, exhibiting unusual initiative and resourcefulness in overcoming the difficulties inseparable from original research. His cheerful disposition never deserted him under the most trying conditions and his relations with his colleagues were of the most cordial kind. He always strove to uphold the traditions of his Alma Mater and often became eloquent in insisting upon how much he was indebted to his chemical teachers at Leeds. The characteristics portrayed in this description would appear to have been retained in undiminished measure in the later period of his life, and his fellow chemists deplore the loss of a colleague whose integrity and sincerity were universally acclaimed.

H. M. Dawson.

ROBERT LLEWELLYN TAYLOR.

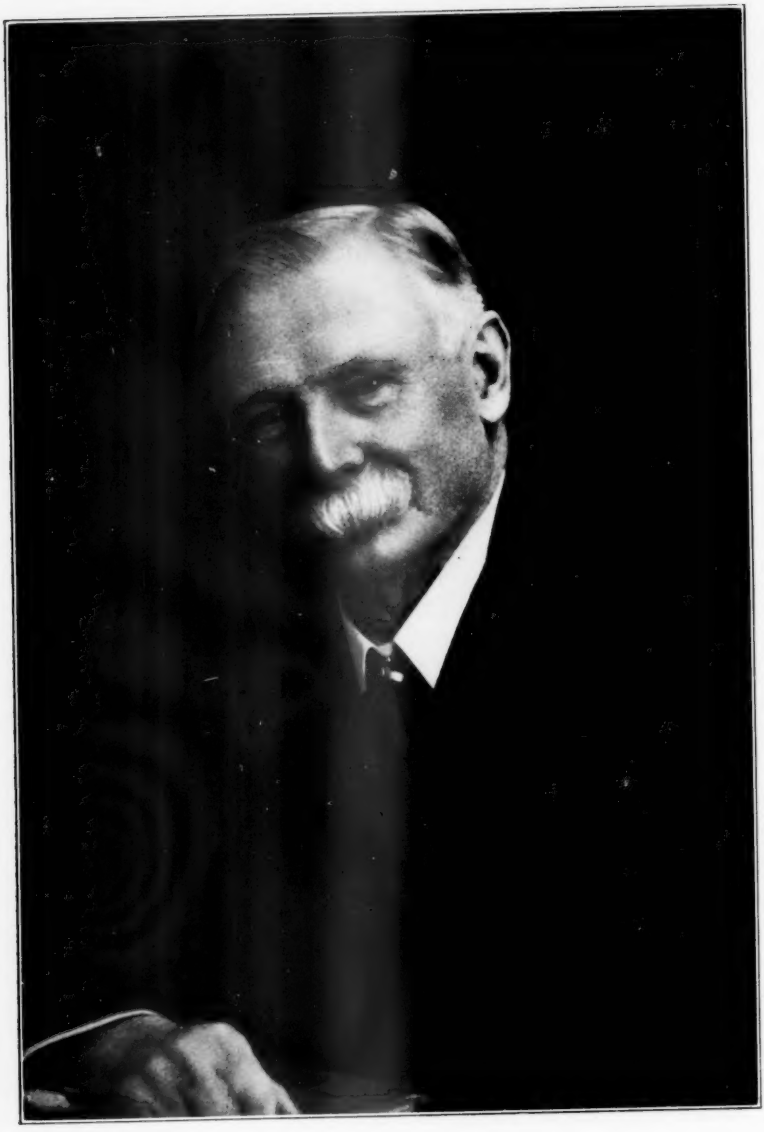
Born November 21st, 1851; Died November 8th, 1925.

One of the pioneers of the teaching of science in this country and a man of high scientific attainments, R. L. Taylor passed away at his home in Whalley Range, Manchester, after a sudden heart attack. He will be sadly missed by many friends and associates, who welcomed a meeting with Taylor as one of their real pleasures. Always enthusiastic in the pursuit of chemical knowledge, of a cheery and kindly disposition, he carried a warm atmosphere about with him.

Taylor was born at Sabden in the Pendle Hill district and as a boy he attended the village school there. At fourteen years of age, he was employed at the print works at Sabden, of which his father was the manager. His parents originally intended that he should learn the business of a calico printer and during four years he spent the daytime in this way. In the evenings he studied the science of chemistry and fitted up a disused room in the works as a chemical laboratory. The course which he followed was no easy one, for he had no teacher, but it was at the same time a fine training ground, because it enabled him to understand the difficulties of others when in later years he became a teacher. After his four years' work at Sabden, he was appointed lecturer's assistant to Dr. A. W. Williamson, Professor of Chemistry at University College, London. Here Taylor made the most of the fine opportunity which presented itself of acquiring skill in experimental and research work. In 1872 he was appointed assistant master in the

chemical laboratory of the Manchester Grammar School and in this position his teaching ability soon made itself manifest. Taylor was associated with Mr. Francis Jones at the Grammar School in the discovery and investigation of boron hydride and the work was published in the *Journal* of the Chemical Society. In 1878, Taylor became teacher of chemistry and physics under the School Board and later he became organising master and inspector of science classes to the Manchester Education Committee. The work from 1880 to the date of his retirement under the superannuation act in 1919 involved both day and evening class duties. In spite of this, he managed to find time for many original investigations and his pupils could realise that they were receiving not merely book lore, but first-hand knowledge from one who worked for the love of science. His research was not made easy by the possession of a well-equipped chemical laboratory and he was always grateful for the encouragement of friends and for the assistance afforded by the loan of some simple piece of apparatus. The records of some of his work appear in the *Transactions* of the Chemical Society, in the *Journal* of the Society of Dyers and Colourists, and in the *Memoirs* of the Manchester Literary and Philosophical Society. They embrace a very exhaustive study of bleaching powder and its action in bleaching, the action of bleaching powder on various natural colouring matters, the effect of light on solutions of bleaching powder, a comparison of the bleaching action of hypochlorous acid and chlorine, and a method for the determination of chloric acid and chlorates. In 1911 he was awarded the research medal of the Worshipful Company of Dyers. In earlier years, Taylor introduced a method for the separation of cobalt and nickel and carried out work on a higher oxide of cobalt and on white ferrous ferrocyanide. His chemical text-books are widely known and include "Analytical Tables for Chemical Students," "Chemistry for Beginners," "The Student's Chemistry," and "Chemistry for Evening Continuation Schools." In 1922 Taylor issued and edited a small book, entitled "Bleaching Powder and its Action in Bleaching," embodying his original memoirs on the subject of bleaching powder.

Many distinguished scholars owe their first inspiration to the teaching and guidance of Taylor. In addition to his scientific attainments, he was able in his leisure hours to provide entertainment for old and young by his lectures and demonstrations such as those on soap bubbles and methods of obtaining a light. With a lively party of boys he would explore the wonders of Castleton, the beauties of Ingleton, and the mysteries of Whalley. His interest in the subject of sound extended still further his love of



Yours very truly
F. S. Peabody

[*To face p.* 1031.]

music and he conducted an orchestra in the Central High School in Manchester.

There is a vacant place in the Manchester Literary and Philosophical Society, of which he was a member of the Council. He was a member of the Chemical Society from January 1874 until the date of his death. [The late] EDMUND KNECHT.

SIR EDWARD THORPE.

BORN DECEMBER 8TH, 1845; DIED FEBRUARY 23RD, 1925.

IN the death of Sir Edward Thorpe, which took place at Whinfield, his residence at Salcombe, South Devon, on February 23rd, 1925, in his eightieth year, the Chemical Society lost a former President, whose membership extended over 54 years, and who during this period served the Society as Member of Council, Vice-President, and Treasurer for ten years, from 1899—1909. The record of Sir Edward Thorpe's activities and achievements in chemistry is a full and varied one. Successively he filled with distinction and success the Chair of Chemistry in three institutions. He was appointed to the Andersonian College, Glasgow, in 1870, having as forerunners Birkbeck, Gregory, and Graham, "an honourable and distinguished ancestry," of which he was justly proud. Then in 1874 Thorpe was appointed Professor of Chemistry in the newly-founded College at Leeds, the Yorkshire College of Science, as it was at first styled, the second of those provincial colleges which owed, in no small measure, their formation to the stimulus which the success of Owens College, Manchester, had given to the movement for the provision of university education in the provinces. This appointment must have appealed especially to Thorpe, himself a first and one of the best products of the provincial university college, affording, as it did, opportunities of putting into practice the system of educative work of which he had had experience in the years spent at Owens College. At that time (1873) Owens College had just emerged from its temporary housing to occupy the first block of buildings on the present site of the University of Manchester. Thorpe was fortunate in having as colleagues men so distinguished as Green, Miall, and Rücker, with whom he laid the foundation and traditions of an institution from which the University of Leeds has grown. When in 1885 Thorpe resigned the post at Leeds to become the successor of Sir Edward Frankland at the Royal College of Science in London, he had the satisfaction of seeing the Yorkshire College housed in new and appropriate buildings, with well-designed and equipped chemical

laboratories and lecture theatres. In the year 1894 he was appointed the Director of the Government Laboratories and was responsible for their design and equipment. Shortly before his retirement, in 1909, he accepted the invitation to resume the Professorship of General Chemistry at the Imperial College of Science and Technology, which had been formed by the amalgamation of the Royal College of Science and the City and Guilds Institute at South Kensington. This position he finally resigned in 1912.

The discharge of the duties of these various positions, and the demands made on his time and energy in the building up of a new college at Leeds, did not prevent Thorpe from maintaining a steady output of scientific investigations and research. Furthermore, throughout his life, he maintained a literary activity; the volume of collected essays on Historical Chemistry, the memorial lectures on Kopp, Victor Meyer, Cleve, and Thomson, as also the articles on scientific worthies contributed to *Nature*, constitute examples of the highly valuable additions made to chemical literature and afford illustrations of the clearness in style and the extensive knowledge which characterised his writings. Thorpe's interest in the history of chemistry is shown by the selection of subjects for addresses. At the Leeds Meeting of the British Association in 1890, Priestley, Cavendish, Lavoisier, and *La Révolution Chimique* formed the subject of the address delivered to Section B (Chemistry) on that occasion; and again, ten years later, he selected for the Presidential Address to this society "The Progress of Chemistry in Great Britain and Ireland during the Nineteenth Century." Further, among other valued contributions to chemical literature are the biographies of Priestley, Davy, and of his teacher, Roscoe.

In more prosaic fields, mention should be made of his text-book of Inorganic Chemistry, published in two volumes, the text-books of quantitative and qualitative analysis, and of the monumental work, "The Dictionary of Applied Chemistry," the preparation of a new and enlarged edition of which occupied him to within a few weeks of his death.

Thomas Edward Thorpe, the son of George Thorpe, a Manchester merchant engaged in the cotton trade, was born on December 8th, 1845, at Barnes Green, Harpurhey, near Manchester. His early education he received at the Manchester Diocesan School (Hulme Grammar School), and in 1863 he entered Owens College as a student in the Chemical Department under Professor Roscoe. Here he remained for four years, acting for the greater part of this period as private assistant to Roscoe, taking an active part in the photochemical researches, the investigation of perchlorates, and in the classical work on vanadium, which ultimately resulted in

assigning to this element its true position in the classification of the elements. In the obituary notice of Sir Henry Roscoe, Thorpe has given an account of much of the work of this period, and in connection with the vanadium investigation he wrote: "It was the writer's privilege to assist in the early stages of this investigation, and it fell to his duty to carry out the various experiments which eventually served to establish the composition of the oxides of vanadium, the true nature of its volatile chlorides, the existence of hitherto unknown oxychlorides, and of the mononitride which Berzelius regarded as the metal, and lastly to fix its real atomic weight and to show that it was apparently 16 units below that assumed by Berzelius on the mistaken supposition that vanadium compounds were analogous in composition to those of chromium."

In connexion with the photochemical researches, Thorpe journeyed in 1866 to Pará on the Amazon, and in the autumn of 1867 he made a long series of observations under a cloudless sky at Moita, near Lisbon, concerned with the relation between the sun's altitude and the chemical intensity of daylight. It was on the return journey from Pará that he made a series of determinations of the carbon dioxide present in the air over the ocean, and succeeded in establishing a constancy in the daily and nightly proportion of 3 volumes of carbon dioxide per 10,000 volumes of air, thus confuting the conclusions drawn by Lewy, who maintained that the proportion of carbon dioxide in the air over the ocean exhibited a diurnal and nocturnal variation. In recognition of this work Thorpe was awarded the Dalton Scholarship in Chemistry.

Mr. J. Kentish Wright of Nottingham, a fellow student and life-long friend of Thorpe, has furnished the writer with the following recollections:

"I first came into intimate association with Thorpe (then universally known as Tom Thorpe) in the year 1865 when we were both students at Owens College, Manchester, and were elected joint Secretaries of the Students' Union. Previous to this I had only known him slightly, as he was entirely a 'science' student, and I was entirely an arts student; as far as I remember, we never attended the same lectures but were constantly meeting on union matters; we soon found we had many tastes and interests in common. He was widely read in modern literature and had a very keen appreciation of Dickens and Thackeray, and we had many talks as to our favourite novels. His distinguishing characteristic was his extraordinary vitality and energy, which he put into whatever he was occupied with, and which enabled him to excel in whatever he undertook. Of his eminence in science I was then and am now unable to judge, but the distinction he attained is sufficient

evidence of this. He was, moreover, a skilful writer of popular sketches and verses, which appeared in the Students' Magazine, and was the author of a very interesting account of the rubber gatherers of South America.

"He had a very strong sense of humour and love of fun, was an excellent story-teller, and could enjoy a joke against himself.

"He was an ardent sportsman and lover of athletics, and took a very active part in originating the boat races, which were rowed on the Irwell between the Science and Arts students. These were started in 1864 and continued for many years. He coxed and coached the Science boat, and on one occasion, although of small stature, he rowed bow in that boat.

"He was also a keen cricketer and a useful bat, playing regularly for the college eleven.

"About this time he introduced me to the young lady (Miss Emma Watts, daughter of Dr. John Watts) to whom at that early age he was engaged and to whom he was devoted the whole of his life. They were married in 1870, at the Manchester Cathedral, and I was present as one of his groomsmen. Lady Thorpe is now living at his beautiful home at Salcombe, South Devon.

"In later years his great pleasure was yachting, and he has written several books describing his cruises. It was soon after he went to Glasgow (about 1871 or 1872) that he bought a small cutter yacht and invited me to go with him on a cruise to the Hebrides. I was terribly disappointed that I could not accept, but subsequently I had reason to congratulate myself. Thorpe sailed the yacht up to Skye and anchored off the coast there—but the wind got up in the night—the anchors dragged and the boat was driven on the rocks and became a complete wreck. There was a small dingy and in this Thorpe and his brother-in-law, Harry Watts, and the two men forming the crew managed to reach the shore. If I had been there, in all probability the dingy would not have carried all and there would have been a tragedy. They spent the night shivering on the rocks, and in the morning found themselves in the most desolate part of Skye—eight miles from the nearest house.

"Although our paths diverged in after life, we kept up our friendship to the end of his life by correspondence and occasional visits. It was always an unfailing delight, when we met, to recall the old days and to tell over again the old stories and reminiscences. The last time I saw him was in the year 1921, when he stayed a few days with me on his road to Edinburgh for the British Association Meeting. Thorpe told me an amusing story about Lloyd George, whom, by the way, Thorpe much resembled in stature and

appearance, and for whom he was often mistaken. Lloyd George, when Chancellor of the Exchequer, wished to put a tax on petrol or other spirits used for motors, and sent for Thorpe, who was then Government Chemist, to obtain the proper word to comprise petrol, benzoline, paraffin, and anything else used for that purpose. Thorpe disapproved of the proposed tax, and determined not to help Lloyd George. He said, 'There is no one in England knows more about it than I do, and I can't find a word, and if I can't, no one can.' Lloyd George jumped up and ran to Thorpe and seized him by the lapels of his coat and shook him vigorously, saying, 'Look here, you can help me and you've got to help me—you can help me and you've got to help me.' Thorpe went away quite won over by Lloyd George's fascination and powers of persuasion. He spent a sleepless night pondering the problem, and with the dawn there flashed across his mind the phrase 'Motor Spirit,' which was accepted and has been in use ever since."

In *The Old Owensian Journal* for May, 1925, appeared an appreciation of Sir Edward Thorpe from the pen of the late Francis Jones, who wrote as follows:

"It was my good fortune to make the acquaintance of T. E. Thorpe in 1866 when I returned from Bunsen's laboratory in Heidelberg to become private assistant to Professor Roscoe in the Old Owens College in Quay Street.

"The Professor told me that he had obtained from the copper works at Alderley Edge a large quantity of a residue containing about 2% of vanadium, and he wished to make an investigation of the properties of that rare element and its compounds. He asked me to work at this along with T. E. Thorpe, who had been a senior student of the College, and I was soon after introduced to him. Thus began a lasting friendship between us, and for many months we worked together on what was to both a most fascinating research. We soon found out that what Berzelius considered metallic vanadium was really the lowest oxide, and this involved the lowering of its combining weight to 51·2. It was impossible to work in daily association with Thorpe without being attracted by his unfailing cheerfulness, genial humour and intimate knowledge of chemistry. The results obtained in the investigation were communicated by Roscoe in a paper read before the Royal Society. Our close association ended in 1867, when Thorpe went to Bunsen's laboratory, and soon after (1870) he became Professor of Chemistry in the Andersonian Institution in Glasgow, but we continued to meet from time to time and kept in touch with each other by correspondence.

"He helped me greatly in 1911 when I started a movement to

celebrate the centenary of Bunsen's birthday by sending an illuminated address and wreaths to the Pro-Rector of Heidelberg University, Professor von Duhn, who requested Bunsen's successor, Professor Theodor Curtius, to acknowledge the address and wreaths which were forwarded to Heidelberg in time for the celebration of the anniversary on March 31st, 1911.

"Professor Curtius wrote: 'The address will be framed and find its place in the Bunsen Room of the Chemical Institute with the picture and other mementos of the Master.' Thanks to Thorpe's help twenty-three former students of Bunsen's added their names to the address; these included Henry E. Roscoe, 1852—1855, Alex. Crum Brown, 1861—1862, W. Marshall Watts, 1865, Francis Jones, 1865—1866, T. E. Thorpe, 1867—1870, C. A. Burghardt, 1870, W. Carleton Williams, 1871—1872, J. Grossmann, 1872—1873, Arthur Schuster, 1872, Arthur Smithells, 1883, and G. H. Bailey, 1884—1885.

"I last saw Thorpe when he was President of the British Association in Edinburgh, when he was unfortunately unable, owing to illness, to be present at most of the meetings."

As has been already mentioned, Thorpe obtained the Dalton Scholarship in Chemistry and then proceeded to Heidelberg to study under Bunsen. The following is an extract from a letter published by Sir Henry Roscoe in his Autobiography from Thorpe in which he describes incidents of his arrival at Heidelberg and his reception by Bunsen:

"Well, in the autumn of '67 I set out for Germany, fortified with much good advice, and bearer of sundry presents from you and yours to Bunsen—among them a copy of *The Times* containing an account of a 'horrid murder' (you remember the dear old man's amiable weakness for 'horrid murders'), a small consignment—I think from Mrs. Roscoe, your mother—of potted shrimps (another amiable weakness), and above all some magnificent specimens of potassium and sodium (calculated to go straight to his heart) from Mather's works at Patricroft. Sonstadt had worked out Caron's process for the manufacture of magnesium, and there was what we then considered a great demand for the metals of the alkalis.

"After a leisurely journey up the Rhine—I remember seeing the white-coated Croats in garrison at Mayence—I found myself in Heidelberg and lost no time in presenting myself to Bunsen, armed with the copy of *The Times*, the potted shrimps, and the precious box containing the alkali metals. Although it was still vacation time, Bunsen had returned to work. I was ushered into the little room you know so well, overlooking the Wrede Platz. The great man—great physically as well as intellectually—rose from

the table at which he was writing—I see him now—and motioned me to the sofa. He evidently was not unprepared for my coming—I suppose you must have informed him. I duly presented your letter of introduction and, after answering his many tender inquiries concerning you, moved up my heavy battalions. I received a momentary check, however, for owing partly to his slight deafness but much more to my imperfect knowledge of German, he moved across to the sofa the better to hear me and sat down on my hat! I at once brought *The Times*, the potted shrimps, and the alkali metals into action. The 'horrid murder' he would read at bed-time: the potted shrimps would certainly be appreciated in the morning: and we prepared ourselves for the alkali metals. The servant was called to unpack the box, when to my consternation he produced a bottle—I remember it was an old pickle-bottle—partially filled with naphtha, at the bottom of which were a few tablespoonfuls of a bright shining rather mobile fluid. I had given the Geheimrath such a glowing account of the size of the sticks of the two metals that I was simply speechless with astonishment and felt indeed rather like an impostor. I had never realised so vividly before the possibility of the transmutation of metals. 'Well,' I said at last, 'potassium and sodium were certainly put into the bottle before I left home, but what is there now is uncommonly like quicksilver.' 'No,' said Bunsen, who was holding the bottle, 'it is not quicksilver. Feel the weight of it!' The fact was that our old friend Heywood, who had been ordered by you to pack the specimens at the time in separate bottles, perceiving that both could be got into one bottle, had, with the charitable idea of not encumbering me with too bulky a package, placed the two metals together, with the untoward result I have indicated. Chemical combination between solids is not of frequent occurrence, but that it is possible under certain circumstances has never been forgotten by me. I had no knowledge at the time of the existence of the fluid alloy—nor had Bunsen—which, perhaps, is not very creditable to us, since it is actually mentioned by Davy. As an historical fact, I believe the first so-called potassium isolated by Davy was fluid at ordinary temperatures owing to the amount of soda in the electrolysed potash.

. . . . . .

"I assure you I felt a little limp at the moment—more limp, indeed, than my crushed hat—and, conversation flagging, he suggested that he should show me the place where he intended that I should work. It was in his own little laboratory, a couple of benches away from him, and where I had as companions Victor Meyer and an American—Gideon Moore—a man of extraordinary

ability, who had the misfortune to be stone-deaf, but who taught himself German and spoke it fluently without having heard a sound of the language."

Thorpe's memorial lectures on Kopp and Victor Meyer enable us to gather something of the impressions made by the life and work at Heidelberg. His fellow students included many whose names are writ large in chemical literature, *e.g.*, Erlenmeyer, Ladenburg, Horstmann, Ludwig, Cohen (the mineralogist), Rose, and Emmerling. Thorpe was undoubtedly greatly attracted to Kopp, whose influence and teaching are to be seen in his own researches on specific volumes and other physical constants, remarkable for their exactitude.

At Heidelberg he graduated as Ph.D., and during this period he published papers dealing with (1) nontronite, to which he assigned the formula $Fe_2O_3,3SiO_2,5H_2O$, (2) the analysis of the ash of a diseased orange tree, and (3) observations on the physical properties of chromium oxychloride, directing attention to the identity in the molecular volumes of sulphuryl chloride (SO_2Cl_2) and chromium oxychloride (CrO_2Cl_2). From the latter he obtained, by the action of heat, the solid oxychloride of chromium–chromium chlorochromate, $Cr_3O_6Cl_2$.

From Heidelberg Thorpe went to Bonn, and whilst there, worked with Kekulé on ethylbenzoic acid, which they isolated from the product of the action of carbon dioxide on sodium and an ethereal solution of ethylbromobenzene.

Returning to Manchester he joined, for what proved a short period, the teaching staff of the chemical department at Owens College, and in 1870 he was appointed Professor of Chemistry at the Andersonian College, Glasgow. Here the association with Young, the founder of the Scottish oil industry, led to the study of paraffin, and in conjunction they conducted a research on the action of heat and pressure on paraffin, which formed the subject of two papers. The authors noted but little gas to be produced, and from 4·5 kilograms of paraffin they obtained 4 litres of liquid hydrocarbons, which were separated into 2·7 litres boiling at 200—300°, 1 litre boiling at 100—200°, and 0·3 litre boiling below 100°. From this last fraction both amylene and hexylene were isolated.

Whilst at the Andersonian College Thorpe attempted, in the light of his experience with vanadium oxychloride, to prepare a lower oxychloride of phosphorus by submitting phosphorus oxychloride to the action of reducing agents, but found the phosphorus compound to behave quite differently, yielding phosphorus trichloride only, and giving no indication of the formation of oxychlorides similar to those of vanadium. The production of phos-

phoryl thiochloride by the interaction of phosphorus pentasulphide and carbon tetrachloride was noted. The determination of the solubility of silver chloride in concentrated nitric acid led to the conclusion that this solubility is of the order of 2 parts of silver chloride in 100,000 parts of concentrated nitric acid. During the tenure of the professorship at Glasgow Thorpe published the text-books already referred to: (1) Inorganic Chemistry, in two volumes (Collins), (2) Quantitative Analysis (Longmans), and (3) Qualitative Analysis; in the production of this last M. M. Pattison Muir collaborated.

The translation to Leeds took place in 1874, when Thorpe was appointed Professor of Chemistry in the Yorkshire College of Science, with A. W. Rücker in the Professorship of Experimental Physics (with which was associated Mathematics) and A. H. Green in the Professorship of Geology and Mining. In the biography of Sir Henry E. Roscoe, Thorpe gives a sketch of the history of the foundation of the Yorkshire College, from which may be gathered some idea of the conditions under which a beginning was made. He writes:

"The premises in which the College was first housed consisted of a disused Bankruptcy Court situated in Cookridge Street, one of the main thoroughfares leading out of the town. After a somewhat chequered career, the building had been partially used as a school of cookery, with the unfortunate result that it had been largely consumed by a fire just prior to being taken over by the College authorities. Although not so spacious as Richard Cobden's old house in Quay Street, Manchester, in which Owens College first started, the Leeds building, in some respects, was not ill-adapted to the purposes of the limited professoriate with which the Yorkshire College of Science began its operations. At all events, it accommodated without the slightest difficulty all the students who sought admission to it on its opening day.

"The College began its work of teaching on October 26th, 1874—somewhat later than the normal opening of a session—owing to delays in completing the necessary structural arrangements. But as there was no yearning anxiety on the part of anybody to learn, no special inconvenience or disappointment resulted. There was no preliminary flourish of trumpets—hardly so much as an opening speech. The initial ceremony was as simple as the appointments of the College were modest. Each of the three professors in turn gave an introductory lecture to an audience consisting of members of the Council and such of the friends of the embryo institution as cared to attend. Some encouraging remarks were made by the Chairman, and so the College was launched. But for a time the

students were few and their advent as far between as the visits of angels."

Unless one has had the like experience, it is not easy to realise what the first years of such pioneering work meant and entailed. However, the work evidently progressed, as in 1877 the foundation stone of the new College buildings was laid, and before this the professoriate had been extended by the appointment of Professor L. C. Miall to the Chair of Biology, and later the establishment of Chairs of Classical Literature and History, and Modern Literature and History, to which Professor J. Marshall, M.A., of Balliol College, Oxford, and Professor F. S. Pulling, B.A. (Oxon), were, respectively, appointed. "This enlargement," Thorpe writes, "of the educational work of the College necessitated a slight but significant change in its designation: henceforward it became known as the Yorkshire College until it was raised to the rank of a university, when it took the name of the town in which it was situated."

The eleven years spent at Leeds were marked by a steady output of scientific work, and this despite the many and varied demands upon Thorpe's time and energy necessitated in establishing the new College. Amongst the researches of this period, researches marked by the accuracy characteristic of all Thorpe's work, are those concerned with the specific volumes of liquids. He was led to conclude from the specific volumes of phosphorus oxychloride and thiochloride that in these compounds phosphorus functions as a tervalent element, thus giving support to the formula $\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!P\!-\!O\!-\!Cl$ in preference to the formula $\begin{matrix}Cl\\Cl\\Cl\end{matrix}\!\!>\!P\!=\!O$, necessitating a quinquevalent phosphorus. A few years later Thorpe was destined to provide evidence in support of the higher valency for phosphorus, by the discovery of the gaseous pentafluoride, as a product of the interaction of arsenic trifluoride and phosphorus pentachloride. The physical properties of this compound afforded a ready means of fixing its molecular weight, which with its analysis showed the molecular formula to be PF_5.

In a lecture to this Society, Thorpe, in 1880, gave an account of his work "On the relation between the molecular weights of substances and their specific gravities when in the liquid state." In recognition of the value of these researches he was awarded the first Longstaff Medal in 1881. Professor Roscoe, the President, in making this presentation, expressed himself as follows:

"Professor Thorpe: I consider it a special privilege that it falls to my lot to present to you, as one of my oldest and most distinguished pupils, the first Longstaff Medal awarded by the

Chemical Society for the best series of original investigations in chemistry published in England during the past three years, amongst which I may mention, as the most important, your discovery of phosphorus pentafluoride; that of the occurrence of heptane in *Pinus Sabiniana*, giving accurate determinations of its physical constants; and, last, the valuable contributions to Physical Chemistry in your researches on the relations between the molecular weights of substances and their specific gravities when in the liquid state. I trust that this recognition by the Chemical Society of your varied and successful labours will stimulate to further efforts, and that before long the Society may be benefited by other communications from your laboratory."

Amongst the communications from the laboratory of the Yorkshire College are to be found: "A Simple and Expeditious Method of Preparing Pyrogallol for Dry Plate Development"; "The Action of Zinc, Magnesium, and Iron as Reducing Agents with Acidulated Solutions of Ferric Sulphate"; "Note on the Action of the Oxychloride of Sulphur on Silver Nitrate"; "Contributions to the History of the Mineral Waters of Yorkshire"; and "On Dust Explosions in Collieries." Further, the re-determination of the atomic weight of titanium was made by Thorpe on the eve of his departure from Leeds. The memorable series of lectures delivered by Thorpe and his colleagues, under the auspices of the Gilchrist Trust, was published in 1878 and edited by him with the title "Coal, its History and Uses."

Considerable activity in research marked the nine years (1885—1894) of the Professorship at the Royal College of Science, as shown by the papers published, conjointly with others, during that period. The determination of the atomic weight of silicon, with J. W. Young, and of gold, with A. P. Laurie, gave the values 28·3 for the former and 196·7 for the latter of these elements. The investigation with Hambly of the vapour density of hydrofluoric acid, proved the density gradually to diminish between the temperatures of 26° and 88°, and, whilst establishing the correctness of the formula HF, demonstrated that it exhibits association similar to that shown by acetic acid and nitrogen peroxide. With Hambly, Thorpe also prepared gaseous phosphoryl trifluoride, which is produced by heating cryolite and phosphorus pentoxide, and showed it to have the molecular formula POF_3. With J. W. Rodger, the corresponding sulphur compound, PSF_3, was prepared by the action of phosphorus pentasulphide on lead fluoride. The investigation, made with A. E. H. Tutton, of the changes involved in the burning of phosphorus in a limited supply of air led to the recognition of phosphorus tetroxide, and the isolation of phosphorous oxide, the

true nature of which, as an easily fusible (melting at 22·5°) and readily volatile compound, was established. The authors succeeded in obtaining this substance in crystalline form and showed from the vapour density the molecular weight corresponded to the formula P_4O_6. A thorough and complete examination of the physical and chemical properties of phosphorous oxide was made, and with the aid of Sir Lauder Brunton its physiological properties were studied, from which it would appear that this compound is the responsible agent in the production of match-makers' disease.

Amongst other publications of this period to be mentioned are: "The Decomposition of Carbon Disulphide by Shock" (a lecture experiment); a lecture experiment to illustrate the phenomena of coal-dust explosions; diethylphosphorous acid (with North Barker); fluosulphonic acid (with W. Kirman); and with L. M. Jones the thermal expansion of specific volumes of certain paraffins and paraffin derivatives. In 1893, the determination of the thermal expansion of liquids formed the subject of a paper read before the Chemical Society. In 1894, with J. W. Rodger, he published a paper on "The Supposed Relation between the Solubility of a Gas and the Viscosity of its Solvent," followed some years later by an account of a research on the viscosity of miscible liquids.

In March, 1894, Thorpe forsook the academic sphere to take up the post of Government Chemist, returning fifteen years later when for three years he took over the duties of Professor of General Chemistry in the Imperial College of Science and Technology. It was after his return to South Kensington that he, with A. T. Francis, made a determination of the atomic weight of strontium.

The writer is indebted to Mr. E. Grant Hooper for the following account of the Government laboratories and of Thorpe's administration and other activities whilst Director.

"This post, to which Thorpe was appointed in 1894, was instituted with the stated object of combining the chemical departments of the Inland Revenue and the Customs, then two separate Services. Both laboratories were originally founded for purely Revenue purposes, but whilst the Customs Laboratory staff continued to be occupied solely with such work, the Inland Revenue Laboratory had been invested with special functions such as Referees under the Adulteration of Food and Drugs Acts and, in addition to Revenue work, had for many years acted as the chemists and chemical advisers of nearly all the other Government Departments. Very large numbers of samples of the widest diversity had been annually examined for the Post Office, the India Office, the Admiralty, the Office of Works, and other civil establishments, and the 'Somerset House Laboratory,' as well as advising in other

capacities, had settled the specifications and examined the stores purchased for official use with the exception of explosives, which were dealt with at Woolwich. The 'Inland Revenue Laboratory,' as its official title was, had thus a very wide experience and its staff in 1894 consisted of a chief and deputy, two superintending analysts, five analysts (1st class), seven analysts (2nd class), and forty-five assistants.

"The Treasury decided that the Inland Revenue and Customs Laboratories should be united under the headship of the 'Government Chemist,' who should be paid from the Treasury Vote, although the staff in each case remained members of their original Departments. This continued for several years, but in 1911 a separate establishment, known as the Government Chemists' Department, was created, to which the staff was transferred except for a certain number of young men belonging to the now united Departments of 'Customs and Excise' and who were and are constantly employed on the more simple revenue determinations. The chemical staff at Somerset House had long outgrown its accommodation, and the development of fiscal business, demanding increased room for clerical work, necessitated the removal of the laboratory. The Treasury therefore determined to provide space elsewhere, and almost immediately after his appointment Thorpe and his staff were called upon to design a new laboratory which it was ultimately decided to build just outside Clement's Inn and closely adjacent to the Law Courts and the newer Bankruptcy Buildings. The new Laboratory, a commodious building admirably adapted for the very extensive chemical work, was brought into use in October, 1897. To this building the Inland Revenue staff was transferred, whilst the laboratory at the Custom House was continued for the examination of the more simple and routine Customs or import samples. It is probably little realised how large a proportion of the huge revenue derived from alcohol (now approximately £153,000,000) and from tobacco (now, say, £53,000,000) is really controlled by scientific work. The charging is, of course, done locally by Customs and Excise officers, but the maintenance of the regulations against the use of forbidden materials and adulteration and the checking of exact strengths or proportions wholly depend upon laboratory examination, whilst the assessment of 'drawback,' *i.e.*, the duty returned on exportation or the allowances for waste material destroyed or denatured, is similarly a matter of purely chemical and microscopical determination. Fresh developments occur from time to time and a new method of determining the amount of dutiable ethyl alcohol in fusel oil led to Thorpe's first communication to the Chemical Society on official subjects, a

paper entitled 'The So-called Hydrates of *iso*Propyl Alcohol' (J., 1897, **71**, 920), whilst reference may be made to the following papers connected with the everyday work of the laboratory, *viz.*, 'Occurrence of Paraffin in the Leaf of Tobacco' (J., 1901, **79**, 982); 'Carbon Monoxide as a Product of Combustion by the Bunsen Burner' (J., 1903, **83**, 874); 'Estimation of Ethyl Alcohol in Essences and Medicinal Preparations' (J., 1903, **83**, 314); and 'Estimation of Methyl Alcohol in the Presence of Ethyl Alcohol' (J., 1904, **85**, 1).

"Much other work either affecting the public or yielding results capable of other than merely official use was accomplished. For many years there had been a demand for duty-free alcohol which should be less objectionable and if possible cheaper than the duty-free alcohol known as methylated spirit. A committee was appointed, of which Thorpe was a member, which brought into existence what was known as 'industrial duty-free alcohol' and further provided for the special denaturing of spirit in cases where the presence of methyl alcohol or of the impurities in the crude wood spirit used for methylation was objectionable. Industrial alcohol had only half the quantity of crude wood spirit used in ordinary methylated spirit and was free from petroleum spirit, and thus was both cheaper and purer, whilst the wider use of specially denatured alcohol afforded substantial relief to many industries and to the fine chemical trade. Improved alcohol tables were also produced. The official strength of alcohols was 'that indicated by Sikes' hydrometer,' and there was no legal authority to ascertain strength in any other manner. By 7 Edward VII, c. 13, s. 4, authority was given to the Commissioners of Customs and Excise to issue regulations for ascertaining the strength of spirits in terms of the 'proof spirit' defined by 56 George III, c. 140. Tables were prepared showing the specific gravity in air at 60°/60° F. of all strengths of alcohol and the equivalent percentage of absolute alcohol by weight and by volume at 60° F. These tables, printed by the Stationery Office and available to the public, were only published after Thorpe's retirement from the Government Laboratory. Other work of a similar character was connected with sugar. Tables of the specific gravity of solutions of cane-sugar had been published by Bell, Thorpe's predecessor as chief of the Inland Revenue Laboratory, in Part I of his book 'Analysis and Adulteration of Foods,' but on the imposition of the sugar duty tables of the specific gravity of solutions of glucose were necessary to permit of the ready charging of the duty on commercial glucose—such were therefore prepared and brought into use.

"The statutory position of the Inland Revenue chemists as referees

in the case of disputed cases under the Food and Drugs Adulteration Acts has been mentioned. For many years difficulties and disputes had arisen in connexion with milk consequent upon the variation in total solids and proportion of butter fat natural to the commodity as drawn from different breeds of cow and under diverse conditions. It had always been evident that to fix a standard, although it might avoid disputes, was not all gain. On the one hand, a workable standard must be lower than the best quality milk, and it was likely that good milk would be systematically reduced to the level of a standard which might be fixed, whilst, further, the existence of a standard was all in favour of the larger organisations and against the smaller men engaged in the trade, who would probably be without chemists or other skilled assistance. In August, 1901, the Board of Agriculture laid down standards for milk solids below which milk was to be deemed adulterated unless the contrary were proved. As Chief Agriculture Analyst under the Board of Agriculture, Thorpe as chief of the Government Laboratory occupied a similar position as referee in disputed cases arising under the Fertilisers and Feeding Stuffs Acts. Just as in the case of milk under the Adulteration of Food and Drugs Acts, standards were laid down for various products and methods of analysis prescribed as the result of collaboration with a committee of representative official analysts.

"Other work connected with the Board of Agriculture may be indicated by the following Government Laboratory publications: 'Effect of feeding Cotton and Sesame Cake on Butter' (A., 1900, i, 237); 'The Fat of the Egg of the Common Fowl' (A., 1902, i, 295); 'Taxine,' the Poisonous Matter of Yew; 'Interdependence of the Physical and Chemical Criteria in the Analysis of Butter Fat' (J., 1904, **85**, 248); 'A Simple Thermostat for Use in Connexion with the Refractometric Examination of Oils and Fats' (J., 1904, **85**, 257); 'Analyses of Samples of Milk referred to the Government Laboratory in Connexion with the Sale of Food and Drugs Acts' (J., 1905, **87**, 206).

"Two subjects of general interest to the public and on which much work was done in the Government Laboratory were connected with lead in pottery glazes and arsenic in food substances and drugs. The Factory Department of the Home Office were, of course, concerned with cases of lead poisoning in industry and especially in connexion with the pottery trade. Regulations as to employment, medical examination of workers, etc., had long been in existence, but a systematic examination of pottery glazes showed considerable variation in the proportions of lead used and in the degree of solubility of the lead, the latter largely depending upon whether

the lead was used as a readily soluble compound such as white lead or whether a fritt was first prepared and the glaze was compounded with the use of such a ground lead silicate. At first the trade as a whole considered the use of lead imperative, and even when it was shown that it was possible to use a lead silicate of a comparatively insoluble character difficulties were alleged, notwithstanding the fact that it was shown that, in addition to endangering the health of the pottery workers, there was pottery on the market which was a danger to the public users because acid fruits, mint-sauce, etc., extracted quite notable proportions of lead from the glaze. Ultimately the use of leadless glazes was proved to be quite practicable, and where lead was still employed the use of comparatively insoluble lead compounds was stimulated by the Home Office granting a relaxation of the conditions of employment in the pottery industry where glazes with a minimum lead-solubility were exclusively employed. Papers on this subject are as follows: 'Lead Silicates in Relation to Pottery Manufacture' (J., 1901, **79**, 791; 1910, **97**, 2282), and a lecture at the Royal Institution.

"In 1901, the world was startled by several cases of arsenical poisoning in Manchester and its neighbourhood which were proved to be due to the consumption of contaminated beer. It was ultimately proved that these cases were caused by the use of an impure, *i.e.*, an arsenical, sulphuric acid for the conversion of starchy material into glucose, which in turn had been employed as an adjunct to malt in the brewing of beer. Extensive investigation showed that arsenic in small but appreciable proportions was widely present in beer; malt itself was found to be contaminated in many instances, such contamination arising from the presence of small quantities of arsenic in the coal and coke used for drying the malt on the malt-kilns. The Commissioners of Customs and Excise, having control over the materials used for brewing, were naturally involved and at once issued orders against the use of any material containing arsenic and against the dispatch of beer into consumption if it contained that substance. The Government Laboratory became flooded with samples from all over the United Kingdom, and a Royal Commission was appointed to investigate the subject. Lord Kelvin was Chairman and Thorpe was a member of the Commission. For the rapid determination of the presence of poisonous proportions of arsenic in beer the Reinsch test had been first used. Thorpe demanded of his staff a gravimetric method, although it was pointed out that the Marsh test afforded a ready means of determination and that the quantities of arsenic so far reported were so small that their separation by a gravimetric method from a liquid like beer, containing relatively large pro-

portions of organic matter, was likely to be difficult. Such a process was, however, worked out and evidence was given before the Royal Commission showing the actual separation of fractions of a milligram of arsenic from quantities such as a pint of beer, and the results of the examination of samples from various parts of the country were furnished. Meantime Local Government Chemists had been mainly using the Marsh test, although not without some trouble consequent on the difficulty at that time of obtaining for the hydrogen-production zinc which was itself sufficiently free both from arsenic, on the one hand, and, on the other, from impurities interfering with the regular evolution of the arseniuretted hydrogen where arsenic was present in the substance under examination. In view of these difficulties and largely under the influence of Lord Kelvin, an electrolytic Marsh test apparatus was devised at the Government Laboratory and put into use. The discovery of arsenic in beer led to an investigation of other materials, not merely brewing substances, malt and sugars, coal and coke used for drying malt, but other substances employed for various purposes, and especially drugs. The result was the revelation of the widespread distribution of arsenic in small proportion and the general recognition of the necessity of laying down standards of purity so that, if absolute freedom from arsenic were not attainable at a non-prohibitive cost, yet both the public and the manufacturers and vendors could be protected by stated maxima. In addition to the evidence published by the Royal Commission, reference may be made to the following papers on this subject: 'Estimation of Arsenic in Fuel' and 'Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials' (J., 1903, **83**, 969, 974); 'Note on the Application of the Electrical Method to the Estimation of Arsenic in Wall-papers, Fabrics, etc." (J., 1906, **89**, 408).

"Another subject affecting public health and especially the health of workpeople employed in the lucifer match industry was that concerned with the presence of white phosphorus in matches. When the use of this substance was forbidden, the detection of small quantities of white phosphorus in the presence of red phosphorus or of other phosphorus compounds became a matter of importance. Hence the paper, 'Note on the Detection of White Phosphorus in the Igniting Composition of Lucifer Matches' (J., 1909, **95**, 440).

"In 1907, the Austrian Government having lent to the British Royal Society certain pitchblende residues, Thorpe undertook the purification of the radium chloride and the re-determination of the atomic weight of radium. A very large number of fractional

recrystallisations of radium chloride were made in the Government Laboratory and the atomic weight 226·7 was deduced in close agreement with Madame Curie's number, 226·2 (*Proc. Roy. Soc.*, 1908, **80**, *A*, 298)."

Thorpe took part in four eclipse expeditions, *viz.*, that of December 22nd, 1870, in Sicily; of July, 1878, at La Junta, Colorado; of August, 28—29th, 1886, at Hog Island, Grenada, West Indies, and of August 16th, 1893, at Fundium, French Senegal. On the last two occasions observations were made on the photometric intensity of light, which formed the subject-matter of two papers published in conjunction with Capt. Abney (*Phil. Trans.*, 1889, **180**, *A*, 368; 1896, **187**, *A*, 423). After the eclipse expedition in 1878 he and Sir Arthur Schuster made a series of magnetic observations in America along the Fortieth Parallel, which were communicated to the Royal Society in a paper entitled, "A Magnetic Survey of the Fortieth Parallel in North America between the Atlantic Ocean and the Great Salt Lake, Utah" (*Proc. Roy. Soc.*, 1879, **29**, 1; 1880, **30**, 132). This was followed in 1880 by a "Note on the Determination of the Magnetic Inclination in the Azores" (*ibid.*, 1881, **31**, 237).

The results of an extensive magnetic survey of the British Isles made in collaboration with his colleague, Sir Arthur Rücker, during the years 1884—1888 formed the subject of the Bakerian Lecture delivered by Thorpe in 1889 (*Phil. Trans.*, 1890, **181**, *A*, 55); and an extension of this work, containing the records of observations at 205 stations throughout the British Isles, constitutes the volume 1896, **188**, *A* of the *Philosophical Transactions*.

Thorpe was elected to the Royal Society in 1876, served on the Council during the years 1890—1891, 1893—1895, and 1899—1903, acted as Foreign Secretary during 1899—1903, and represented the Society on the occasion of the 200th celebration of the foundation of the Royal Academy of Sciences of Berlin. He delivered the Bakerian Lecture on two occasions, in 1889 and 1904, the results of his determination of the atomic weight of radium being the subject of the second lecture. In 1889 he was awarded a Royal Medal. The President of the Royal Society (Sir Gabriel Stokes), in making this award, spoke as follows: "Professor Thomas Edward Thorpe's experimental work has secured for him a place in the first rank of living experimentalists. His researches, which are not confined to one department of chemical science, are all distinguished both by accuracy and originality of treatment. As examples of the high character of his investigations, those of the determinations of the atomic weights of titanium and gold may be specially cited as permanently setting the value of two most important chemical

constants; whilst his researches on fluorine compounds, including the discovery of thiophosphorylfluoride, a body capable of existing undecomposed in the state of gas, and his latest work on the vapour density of hydrofluoric acid, do not fall short of the highest examples of classical chemical investigation."

It was at the Edinburgh Meeting of the British Association in 1871 that Thorpe acted as Secretary of Section B (Chemistry) and fifty years later he was President of the Association at its meeting in the same city. At the Leeds Meeting in 1890, he presided over the Chemistry Section. The Presidential Address at the Edinburgh Meeting which, owing to illness, he was unable to deliver in person, was devoted to a plea for an international ban on chemical warfare. He served on several Royal Commissions and numerous Departmental Committees, was an active member of the International Committee of Atomic Weights, contributing experimental data for the determination of the atomic weights of no fewer than six elements. In 1895 he was elected President of the Society of Chemical Industry.

The record of Thorpe's scientific investigations and achievements shows how abundantly he gave of himself without stint or reserve to the advancement of knowledge, and this with a success indicated in the many recognitions and honours received by him from universities and learned societies both at home and abroad. In 1900 he was made a C.B., and on retiring from the Directorship of the Government Laboratory was knighted. In 1912 he resigned the Chair of General Chemistry at the Imperial College of Science and Technology and went to reside at Salcombe in South Devon, where he had built a house, and there devoted himself to literary work, yachting, and gardening. Sailing remained a lasting source of pleasure to him, and it is characteristic of the man that he should use his pleasure cruises as opportunities for research, as in the case of the magnetic surveys, already mentioned. Further, his yachting experiences were made to provide the material for those literary excursions: "A Yachtsman's Guide to the Dutch Waterways" (Standford, 1905), and "The Seine from Havre to Paris" (Macmillan, 1913). The revision and enlargement of the "Dictionary of Applied Chemistry" occupied him to within a few days of the illness which, as already stated, terminated fatally on February 23rd, 1925.

As to Thorpe's influence and personality, no better testimony is needed than that expressed by Dr. Tutton in the obituary notice published in the *Proceedings of the Royal Society* in December, 1925: "An able and incisive speaker, compelling attention (in spite of his stature) both by his resonant voice and his always interesting matter, a brilliant lecturer and experimenter, a faithful teacher

who never failed to make himself clearly understood, and an original investigator of keen penetration, infinite reserve, consummate manipulative skill, scrupulous accuracy and its ever accompanying quality of neatness, Sir Edward Thorpe not only inspired those who had the good fortune to study under him, but impressed the honourable mark of thoroughness and trustworthiness on the department of British Science which he so well represented. The spirit of research ever emanated from him and vivified all his teaching, and it may be hoped, and indeed believed, that its leaven has quickened the spirit of a band of devoted students, striving to emulate his fine example and to work for the honour of British Science and the acquirement of true knowledge for its own sake, throughout the whole Empire."

In conclusion the writer wishes gratefully to acknowledge the kindness of Lady Thorpe and her niece (Miss Watts) in placing at his disposal documents relating to the life and work of Sir Edward Thorpe.

P. P. B.